

PHASE EQUILIBRIUM IN SYSTEMS CONTAINING FLUOROCARBONS

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CHAPTER I

PURPOSE

The purpose of this work is twofold:

1. The determination of the necessary phase equilibrium data for the evaluation of various methods of separating fluorocarbon mixtures and hydrocarbon mixtures, particular emphasis being given to the methods of liquid extraction, extractive distillation, and azeotropic distillation.

2. The calculation of the thermodynamic properties of some fluorocarbon-hydrocarbon mixtures and the comparison of these calculated properties with properties predicted from various theories of solutions.

CHAPTER II

NOMENCLATURE

a	Activity, standard state taken as pure substance
A	Van Laar constant
B	Van Laar constant
d ⁰	Distance between centers of nearest-neighbor molecules
H	Partition coefficient, defined as the ratio of solute per unit volume of solvent to solute per unit volume of gas phase
I	Ionization potential
N	Number of theoretical plates
p _i	Inlet pressure in chromatography column
p _o	Outlet pressure in chromatography column
p ⁰	Vapor pressure of pure compound
R	Gas constant
T	Absolute temperature, °K.
V	Molal volume, cc
V _g	Volume occupied by vapor phase in chromatography column
V _r	Retention volume, defined as the volume of carrier gas passed through chromatography column when solute peak appears

V_s	Volume occupied by stationary solvent phase in chromatography column
$\tilde{V}_s$	Molar volume of stationary solvent phase, cc
w	Weight fraction
x	Mole fraction
y	Mole fraction of a component in vapor phase
z	Correction factor
ΔA	Change in Helmholtz Free Energy
ΔE	Change in Internal Energy
ΔF	Change in Gibbs Free Energy
ΔH	Change in Enthalpy
ΔS	Change in Entropy
α	Coefficient of thermal expansion
α	Relative volatility
β	Isothermal compressibility
β	Solvent selectivity
γ	Activity coefficient, standard state taken as pure substance
δ	Solubility parameter, $(E^V/V)^{1/2}$ (calories/cc) ^{1/2}
π	Total vapor pressure
ϕ	Volume fraction
θ	Retention time, defined as time for appearance of solute peak

Subscripts

1	}	Refer to components
2		
3		
C		Refers to consolute properties
D		Refers to distillate composition
M		Refers to mixture properties
O		Refers to ideal solution properties
P		Refers to constant pressure process
V		Refers to constant volume process
W		Refers to composition of material in distillation pot

Superscripts

e	Refers to excess properties
M	Refers to mixing process
V	Refers to vaporization process
'	Refers to hydrocarbon-rich phase

CHAPTER III

INTRODUCTION

Before any equipment affecting physical separation of two or more components can be designed, phase equilibrium data must be available. Since the majority of the unit operations involve the contacting of two phases under conditions approaching equilibrium, the determination, correlation, and prediction of phase equilibrium data play an important role in the field of chemical engineering.

A most desirable method of obtaining necessary phase equilibrium data would involve the calculation of the properties of the mixture from those of the pure components; however, to be used with confidence, any such method should have some sound theoretical basis. At present there are several approaches to the theory of solutions, most of which have a statistical mechanical basis and require many assumptions and approximations and yield equations which are complex and cumbersome.

A simple theory that has achieved considerable success in the treatment of solutions of nonelectrolytes is one developed independently by Scatchard and by Hildebrand (11). By making four simple assumptions, Scatchard and Hildebrand

arrived at the following expression for the energy of mixing in a binary system:*

$$\Delta E^M = (x_1 v_1 + x_2 v_2) (\delta_1 - \delta_2)^2 \phi_1 \phi_2 \quad (1)$$

The four assumptions were:

1. The energy of a system can be expressed by summation of the interaction energies of all possible pairs of molecules. This interaction energy was assumed to depend only on the distance between the two molecules.
2. The distribution of molecules is random with respect to position and orientation.
3. There is no volume change on mixing at constant pressure.
4. The interaction energy between 1-2 pairs of molecules is the geometric mean of the interaction energy between 1-1 and 2-2 pairs. Strictly speaking this theory applies only to systems containing nonpolar molecules between which only dispersion forces are operating.

By further assuming that the entropy of mixing has the same value as that of an ideal solution (a solution obeying Raoult's law) it is possible to write for the free energy of mixing

*A tabulation of the nomenclature used in this work is given in Chapter II.

$$\Delta F = (x_1 v_1 + x_2 v_2) (\delta_1 - \delta_2)^2 \phi_1 \phi_2 + RT(x_1 \ln x_1 + x_2 \ln x_2) \quad (2)$$

and for the activity coefficients

$$\begin{aligned} RT \ln \gamma_1 &= v_1 (\delta_1 - \delta_2)^2 \phi_2^2 \\ RT \ln \gamma_2 &= v_2 (\delta_1 - \delta_2)^2 \phi_1^2 \end{aligned} \quad (3)$$

From its inception in 1932 until about 1950 the success of the Scatchard-Hildebrand theory had been measured by its prediction of the properties of hydrocarbon systems. Since 1950 much work has appeared concerning fluorocarbon-hydrocarbon systems which were not adequately accounted for by the theory. These systems have much larger positive deviations from Raoult's law than are predicted. For some systems these positive deviations are large enough so that at room temperature two liquid phases exist.

Because of their nonconformity to the existing theory, fluorocarbon-hydrocarbon systems have stimulated the interest of many investigators. The first comprehensive study of fluorocarbon-hydrocarbon systems was made by Simons and Dunlap (39) followed later by Simons and Mausteller (40); these investigators determined the thermodynamic properties of C_5F_{12} - C_5H_{12} and C_4F_{10} - C_4H_{10} systems respectively.

Simons and Dunlap found the Scatchard-Hildebrand theory to be inadequate in predicting the thermodynamic

properties of their system, and improved the agreement by rederiving equation 1 omitting the assumption of no volume change on mixing. Later Reed (32) showed that for fluorocarbon-hydrocarbon mixtures the interaction energy between unlike pairs of molecules is not the geometric mean of like pairs as was also assumed in the derivation of equation 1. Reed also rederived equation 1 omitting the assumptions of the geometric mean and no volume change. He was able to calculate values of the heat of mixing which agreed very well with the experimental data of Simons and Dunlap, and Simons and Mausteller.

Since most fluorocarbon-hydrocarbon mixtures do not conform to the present theory, their study should prove useful toward further development and evolution of the theory and the understanding of solution processes.

CHAPTER IV

BINARY SYSTEMS FORMING TWO LIQUID PHASES

The study of binary systems forming two liquid phases was undertaken for two reasons:

1. To determine solubility relationships which might be useful in selecting a solvent for separating fluorocarbon-fluorocarbon mixtures and hydrocarbon-hydrocarbon mixtures.
2. To obtain a measure of the positive deviations from Raoult's law exhibited by binary mixtures of two partially miscible liquids.

Experimental.--The properties of the pure compounds used in this study are tabulated in the appendix under Tables VII and VIII.

The unmixing temperature of a known binary mixture was determined by heating the mixture until the two liquids were completely miscible, then cooling the solution slowly and observing the temperature at which the second liquid phase appeared. The appearance of the second phase on cooling is marked by cloudiness; this cloudiness is sometimes masked by an opalescence which occurs about 2 or 3 degrees above the consolute temperature. Due to this opalescence, the determination of the unmixing temperature depends to some

extent on the judgment of the observer.

The solubility apparatus shown in Figure 2 consisted of a heavy-walled glass test tube clamped between two stainless steel flanges by means of four brass bolts. A Teflon gasket placed between the open end of the tube and the top flange was used to seal the tube. A thermocouple, which passed through the top flange, was used to measure the temperature of the mixture. The whole tube assembly was immersed in an oil or water bath, which provided the necessary temperature control.

The solubility data are tabulated in Table XII and the solubility curves, which were obtained by plotting the unmixing temperature-composition data, are shown on Figures 3-7. Published data are available for the two perfluorohexane systems (17); these points are plotted on Figure 3 along with the present data. The agreement between the two sets of data is satisfactory.

Due to the presence of air in the solubility tube, the values of the unmixing temperatures so determined pertain to the mixture saturated with air and at a pressure in excess of the equilibrium vapor pressure of the mixture. The difference between these values and those of the mixture under its own equilibrium vapor pressure is generally assumed to be negligible, but in order to justify this assumption the un-

mixing temperature was determined for a degassed mixture of toluene and perfluorocyclic oxide* in a sealed glass tube under its own equilibrium vapor pressure. This value of the unmixing temperature is plotted on Figure 4 along with those obtained in the presence of air and it can be seen that there is no significant difference.

Theoretical Calculation of Consolute Temperature and Composition.—The thermodynamic conditions necessary to define the consolute temperature are

$$\begin{array}{ccc} \frac{da_1}{dx_1} = 0 & \text{or} & \frac{d \ln a_1}{dx_1} = 0 \\ \frac{d^2 a_1}{dx_1^2} = 0 & & \frac{d^2 \ln a_1}{dx_1^2} = 0 \end{array} \quad (4)$$

This requirement can be seen from examination of Figure 3, where three isothermal curves of activity are plotted versus composition. For illustrative purposes the activity is calculated from the following equation

$$\ln a_1 = \ln x_1 + Bx_2^2 \quad (5)$$

At T_1 , a temperature below T_c (consolute temperature), there exist two liquid phases having the same activity. These

*A description of this material is given in the appendix.

phases correspond to points A and B. The dashed portion of the curve has no physical significance and corresponds to the Van der Waals isotherm in the two phase region on a pressure-volume diagram of a pure substance. As the temperature is increased, the length of the line AB decreases until the consolute temperature T_c is reached and a point of inflection, C, is observed in the activity curve. At this point the first and second derivatives of the activity are equal to zero. At a temperature T_2 , above T_c , the deviations from Raoult's law become smaller and the activity is a single valued function of composition.

The value of the activity as predicted by the Scatchard Hildebrand theory is

$$\ln a_1 = \ln x_1 + \frac{V_1}{RT} (\delta_1 - \delta_2)^2 \phi_2^2 \quad (6)$$

Using equation 6 for the activity and applying the conditions of equation 4, the following expressions result for the consolute temperature and composition.

$$RT_c = \frac{2x_1x_2V_1^2V_2^2(\delta_1 - \delta_2)^2}{(x_1V_1 + x_2V_2)^3} \quad (7)$$

$$x_1 = \frac{(V_1^2 + V_2^2 - V_1V_2)^{1/2} - V_1}{V_2 - V_1} \quad (8)$$

By using the entropy of mixing for molecules of different

sizes as calculated from a lattice model along with the energy of mixing as given by equation 1, Hildebrand (18) derived expressions for the consolute temperature and composition somewhat different from equations 7 and 8

$$RT_c = 2v_1v_2(\delta_1 - \delta_2)^2 / (v_1^{1/2} + v_2^{1/2})^2 \quad (9)$$

$$\phi_1 = \frac{v_2^{1/2}}{v_2^{1/2} + v_1^{1/2}} \quad (10)$$

The consolute temperatures and compositions have been calculated from equations 7 and 8, and 9 and 10 for the systems reported in this work and are tabulated in Table XIII. The values of the consolute composition in Table XIII are given only to two figures because of the uncertainty in locating the composition corresponding to the maximum temperature. From Table XIII it is obvious that equations 8 and 10 predict the consolute composition quite well while equations 7 and 9 provide poor estimates of the consolute temperature. Only for the system perfluorocyclic oxide-toluene was the consolute temperature correctly predicted by equation 7.

The fact that equations 8 and 10 predict the consolute composition would indicate that the volume fraction is a useful variable in correlating solution behavior. This is borne out by the successful correlation of experimental activity

coefficients by the Van Laar equation, which is similar in form to equation 3, but contains two adjustable parameters instead of constants which are fixed by the physical properties of the pure components.

The failure of equations 7 and 9 to predict the consolute temperature is probably due partly to the failure of fluorocarbon-hydrocarbon mixtures to conform to the geometric mean assumption which is implicit in these equations. Equation 9 predicts lower temperatures than equation 7 because the excess entropy of mixing due to different volumes is always positive and therefore the deviations from Raoult's law due to this correction are always negative. Since fluorocarbon-hydrocarbon mixtures show much larger positive deviations than predicted, the entropy correction impairs the agreement between the observed and predicted temperatures. It can not be stated, however, that the use of the entropy term for unequal volumes is incorrect since the small effect it contributes is overshadowed by the larger effect probably due to the geometric mean assumption.

It should be mentioned that, although often used in the literature, comparison of the calculated and observed consolute temperature is not a good criterion for testing the applicability of the Scatchard-Hildebrand theory. If

equations 7 and 8 predict the correct temperature and composition, this means that the first and second derivatives of the true activity coefficient with respect to composition are equal to the corresponding derivatives of the activity coefficient as given by equation 3. This is a necessary, but not a sufficient condition which must be fulfilled by equation 3, for it is conceivable that two different functions could have equal first and second derivatives at a given composition. This reasoning can be substantiated by comparing activity coefficients calculated by equation 3 with experimental values for some systems which conform to the consolute temperature criterion. This is done below.

In a two liquid phase system the activity of a component is equal in both phases and we can write

$$x_1 \gamma_1 = x_1' \gamma_1' \quad (11)$$

In many fluorocarbon-hydrocarbon systems which form two liquid phases the mole fraction of hydrocarbon in the hydrocarbon-rich phase approaches unity at low temperatures and the activity coefficient also approaches unity. Thus by setting γ_1' equal to unity, the activity coefficient of the hydrocarbon in the fluorocarbon-rich phase (γ_1) is equal to the ratio x_1'/x_1 . Values of $\ln \gamma_1$ so calculated are compared in Table I with values predicted by equation 3 for

three systems in which the observed and calculated consolute temperatures are in good agreement.

TABLE I
TEST OF THE CONSOLUTE TEMPERATURE CRITERION

SYSTEM	T_c °K		t (°C)	x_1	x'_1	$\ln \gamma_1$		REF.
	obs.	eq.7				eq. 11	eq. 3	
I	323.5	325	26.3	0.306	0.960	1.14	0.913	19
II	358.5	360	61.1	0.320	0.956	1.09	0.900	19
III	386	377	69.0	0.256	0.981	1.34	0.977	this work

I. perfluoromethylcyclohexane and chloroform

II. perfluoromethylcyclohexane and benzene

III. perfluorocyclohexane and toluene

One would expect the same percentage difference between the logarithm of the activity coefficients as between the two temperatures in Table I since both T_c and $\ln \gamma$ are directly proportional to the $(\sigma_1 - \sigma_2)^2$ term. Inspection of Table I reveals that the percentage difference between the logarithms of the activity coefficients is much greater than between the consolute temperatures. Since the values of $\ln \gamma_1$

and T_c in Table I are compared at different temperatures, the possibility arises that the activity coefficients predicted by equation 3 are equal to the true activity coefficients at the consolute temperature only, and not at other temperatures. From consideration of the consolute temperature alone one would erroneously assume that the three systems in Table I closely conformed to the theory.

CHAPTER V

TOTAL VAPOR PRESSURE OF BINARY MIXTURES

Experimental.--Total vapor pressure versus temperature data were obtained for six binary fluorocarbon-hydrocarbon mixtures. The physical properties of these compounds are listed in Tables VII and VIII.

The measurements were made in the two liquid phase region since liquid compositions could be determined from the temperature and the experimentally established solubility curve.

A dynamic boiling still was used for these measurements, the design details of which should be obvious from examination of Figure 9. The still was designed so that vigorous boiling and low liquid level would prevent superheating while the insulating vapor space would prevent any heat loss by the vapor in the inside tube. During operation of the still under equilibrium conditions no condensation was observed inside the inner tube. A calibrated thermocouple was used to measure the vapor temperature; the calibration data for this thermocouple is reported in Table IX. The still was connected to a vacuum system containing a mercury manometer which could be read to the nearest tenth of a millimeter

by use of a cathetometer.

As a check on the performance of the still the total pressure of the system 2 butanone-water was determined at two temperatures. These values compare favorably with the reported literature values (29) as shown in Table II.

TABLE II

CHECK RUN IN TWO LIQUID PHASE STILL

System: 2 butanone--water reference 29

Literature		This Work	
Pressure mm	Temperature °C	Pressure mm	Temperature °C
760	73.3	768	73.6
500	62.0	503	62.0

The experimental total vapor pressure versus temperature data are reported in Table XIV.

Calculation of Activity Coefficients from Liquid-Liquid Solubility Data.--The following method for calculating activity coefficients has been described by Carlson and Colburn (6). In a two liquid phase system the activity of a component is equal in both liquid phases and we can write

$$x_1 \gamma_1 = x_1' \gamma_1' \quad (11)$$

$$x_2 \gamma_2 = x_2' \gamma_2'$$

The mole fractions are known from the solubility data and we have two equations containing four unknown quantities. The number of unknowns can be reduced to two if it is assumed that a two-constant equation can be found which correctly expresses the activity coefficients as a function of composition. One such equation which has proved useful in correlating experimental activity coefficients is the Van Laar equation.

$$\ln \gamma_1 = \frac{A}{\left(\frac{Ax_1}{Bx_2} + 1\right)^2} \quad (13)$$

$$\ln \gamma_2 = \frac{B}{\left(\frac{Bx_2}{Ax_1} + 1\right)^2} \quad (14)$$

If equations 13 and 14 are substituted into equations 11 and 12 written in logarithmic form, values of the constants A and B can be found. This procedure can be repeated at several temperatures so that the temperature dependence of A and B can be determined. The Van Laar A and B have been calculated for several of the fluorocarbon-hydrocarbon systems for which the solubility curves were determined and it was found that the constants were always linear functions of temperature. Figure 10 shows several of these linear plots.

In order to have confidence in values of the activity

coefficient as calculated from equations 13 and 14, some method should be available for determining whether the Van Laar equation accurately predicts the activity coefficients. One method of accomplishing this is to compare experimentally determined total vapor pressures with those calculated from equation 15 using the vapor pressures of the pure compounds, solubility data, and the Van Laar equation to determine the activity coefficients.

$$\pi = x_1 \gamma_1 p_1^0 + x_2 \gamma_2 p_2^0 \quad (15)$$

A graphical comparison of calculated and experimental total vapor pressures is given in Figures 11-16, where it is revealed that the agreement is quite good at lower temperatures, but becomes poorer as the temperature increases. The fact that calculated and experimental values of the total vapor pressure agree should not be taken as conclusive proof that the activity coefficients predicted by equations 13 and 14 are correct, however, since there is an infinite number of combinations of γ_1 and γ_2 which will satisfy equation 15.

By rearranging equation 15 we see that the activity of component two is a linear function of the activity of component one.

$$a_2 = \pi / p_2^0 - a_1 p_1^0 / p_2^0 \quad (15a)$$

By using equation 15a we can establish limits for the activity of the fluorocarbon (component 2) from the limits of the hydrocarbon activity. The upper limit for the activity of the hydrocarbon will be set at unity and since these mixtures all exhibit positive deviations from Raoult's law, the lower limit will be set at the mole fraction of hydrocarbon in the hydrocarbon-rich phase. Table XV shows the activity limits of the fluorocarbon as determined from equation 15a along with the values calculated from the Van Laar equation for all six systems for which the total vapor pressure was determined. Table XV reveals that for most systems the calculated activities fall within the range calculated by equation 15a at the low temperatures, but deviate at higher temperatures following a pattern similar to the observed and calculated total vapor pressures.

The Van Laar activity coefficients determined from the solubility data of Simons and Dunlap (39) are plotted on Figure 17 along with their activity coefficients determined from partial pressure data for the system perfluoropentane-n-pentane. The value of the total vapor pressure in the two liquid phase region for this system at 262.4°K. , calculated from the Van Laar equation, is 214 mm. as compared to the reported value of 216 mm., and the Van Laar activity of 0.766 falls within the 0.718 to 0.855 range calculated from equation 15a. It can be seen from Fig. 17 that the Van Laar

equation with constants determined from solubility data predicts values of the activity coefficients which agree very well with the experimental ones. The Van Laar equation with constants determined from solubility data has successfully predicted excess free energies of mixing in other fluorocarbon-hydrocarbon systems for which the thermodynamic properties have been determined. Figures 18-20 show that the calculated and experimental excess free energies of mixing for the systems n-perfluoropentane and n-pentane (39), n-perfluorobutane and n-butane (40) and perfluoroheptane and iso-octane (26) are in good agreement. These experimental values of the excess free energy of mixing were determined from partial pressure data.

The solubility data for the system perfluoroheptane and isooctane were taken from reference (17); calculated values of ΔF^G for this system were made from the solubility data and the Van Laar equation at 17° C. while the reported data are at 30° C. The excess free energy data of Simons and Dunlap and Simons and Mausteller are the averages of several temperatures in the ranges 262 to 293° K. and 233 to 260° K., respectively, while those calculated from solubility data are at 262.4 and 220° K. respectively. The small difference in temperature between calculated and observed free energies is negligible since

the temperature derivative of the excess free energy of mixing is the excess entropy of mixing at constant pressure. Values of excess entropy of mixing are tabulated below for several systems.

ΔS_p^e		
System	at $x = 0.5$, cal./mole $^{\circ}\text{K}$	Reference
$\text{C}_4\text{F}_{10} - \text{C}_4\text{H}_{10}$	1.00	40
$\text{C}_5\text{F}_{12} - \text{C}_5\text{H}_{12}$	0.43	39
$\text{C}_7\text{F}_{16} - i\text{-C}_8\text{H}_{18}$	0.24	26

This entropy term does not usually exceed one entropy unit and a change of ten degrees would result in less than a 10 calories per mole change in the free energy term.

The partial molal heat of mixing can also be calculated from the Van Laar equation and the temperature derivatives of its constants

$$\Delta \bar{H}_1 = - \left(\frac{\partial \ln \gamma_1}{\partial T} \right)_x RT^2 = - RT^2 \frac{\partial}{\partial T} \left[\frac{A}{\left(\frac{Ax_1}{Bx_2} + 1 \right)^2} \right] \quad (16)$$

Heats of mixing calculated from the Van Laar equation are approximately twice as large as those determined experimentally in the three fluorocarbon-hydrocarbon systems cited above. Wood (48) has calculated the thermodynamic properties for the system cyclohexane-methanol from solubility data alone, but using a two-constant Scatchard equation instead of the Van Laar equation to represent activity coefficients. He found that his calculated excess free energies of mixing were in line with those reported for the methanol-benzene and methanol-carbon tetrachloride systems, but his calculated heat of mixing values were about twice as large as those for the two reported methanol systems.

Besides the Van Laar equation, two-constant Margules and Scatchard equations were used in this work for substitution into equations 11 and 12, but these equations predicted total vapor pressures that did not agree with the observed vapor pressures as well as did those predicted from the Van Laar equation. These two types of equation also predicted heats of mixing which were in poorer agreement with the experimental values than those predicted by the Van Laar equation.

Since the temperature derivative of the free energy is needed for calculation of the heat of mixing, small errors in the free energy will produce larger errors in the heat of

mixing. The disagreement between experimental heats of mixing and those calculated from the Van Laar equation could be attributed to small errors in the free energy as predicted by the Van Laar equation. However, these errors are not of a random nature since the calculated value is always about two times as large as the experimental values.

In order to determine why the Van Laar equation fails we should consider in detail the process by which the Van Laar constants are determined. Figure 21 illustrates graphically the conditions required to obtain the Van Laar constants. Equations 11 and 12 can be rearranged to

$$\ln \gamma_1 - \ln \gamma_1' = \ln x_1'/x_1 \quad (11a)$$

$$\ln \gamma_2 - \ln \gamma_2' = \ln x_2'/x_2 \quad (12a)$$

The differences $\ln \gamma_1 - \ln \gamma_1'$ and $\ln \gamma_2 - \ln \gamma_2'$ are represented on Figure 21 by ab and cd respectively. Using equations 11, 12, 13, and 14 is equivalent to finding the constants A and B such that at x_1 and x_1' the differences $\ln \gamma_1 - \ln \gamma_1'$ and $\ln \gamma_2 - \ln \gamma_2'$ given by the Van Laar equation are equal to the corresponding differences between the true activity coefficients. This does not mean that the actual values of the Van Laar activity coefficients are correct or that the Van Laar curve is identical with the true

activity coefficient versus composition curve.

At lower temperatures the composition of the conjugate phases approaches that of the pure compounds and the true activity coefficient and Van Laar activity coefficient both approach unity. This means that at lower temperatures the activity coefficients γ_1' and γ_2 corresponding to points a and c on Figure 21 can be predicted by the Van Laar equation. Since the Van Laar activity coefficients and true activity coefficients approach each other at a and c, and since ab and cd as given by the Van Laar equation are equal to ab and cd corresponding to the true values of $\ln \gamma_1 - \ln \gamma_1'$ and $\ln \gamma_2 - \ln \gamma_2'$, the Van Laar and true activity coefficients also approach each other at b and d. This is manifested by the very good agreement between observed and calculated total vapor pressures at lower temperatures. As the temperature increases the concentration of the major component in each phase decreases causing the activity coefficients to differ from unity and it is possible that differences occur between the Van Laar and true activity coefficients at a and c. This would result in differences at b and d and would cause the values of the observed and calculated total vapor pressures to diverge.

One reason why the Van Laar equation does not correctly predict heats of mixing can be seen from examination of

Figure 22. Curves 1 and 2 on Figure 22 represent the Van Laar equation at two temperatures, curve 1 being at the lower temperature. Curves 3 and 4 represent the true activity coefficient curves, where curves 3 and 1, and 2 and 4 are at the same temperatures. Only the curves for one component are shown for the sake of simplicity. The shape of the two types of curves is greatly exaggerated for illustrative purposes. At the temperature T_1 , the Van Laar equation (1) predicts correct values of the activity coefficient at a and b even though its form is different from the true activity coefficient curve (3) at that temperature. Increasing the temperature to T_2 causes only a slight change in the true activity coefficient curve (4), but due to the difference in form the Van Laar curve (2) must change by a greater amount in order that it may predict the activity coefficients at c and d. Since the heat of mixing is determined from the temperature derivative of the logarithm of the activity coefficient at constant composition, it can be seen that larger heats of mixing would be obtained by the Van Laar equation. We see that the inability of the Van Laar equation to predict heats of mixing could be due to a difference in form between the calculated and true activity coefficient curve. This difference is undoubtedly small since the

excess free energy of mixing curves calculated from the solubility data using the Van Laar equation agree in magnitude and in shape with experimentally determined excess free energy curves.

Based on the preceding considerations it is concluded that the Van Laar equation can be used to estimate free energies in systems which form two liquid phases if the constants are determined at temperatures where the compositions of the two coexisting phases approach the pure compounds. Of course more confidence can be placed in the Van Laar equation if total pressure data are available. Since the temperature derivative of the free energy is small, these estimated free energies can be used without appreciable error at other temperatures within 20° or 30° C. of the temperature at which the estimate was made. It is further concluded that the heats of mixing predicted by the Van Laar equation are unreliable.

CHAPTER VI

VOLUME CHANGES IN MIXING FLUOROCARBONS AND HYDROCARBONS

Experimental.---The molal volumes as a function of composition were determined for four fluorocarbon-hydrocarbon systems. The physical properties of the pure compounds are given in Tables VII and VIII. Pycnometers described by Lipkin (22) and having a nominal capacity of 5 milliliters were used to measure the volumes of mixtures of known composition. These pycnometers were calibrated with distilled mercury at 40°, 45°, 50°, and 60° C.; the calibration data are given in Table X.

The molal volumes of the fluorocarbon-hydrocarbon solutions were measured over the entire composition range at a temperature slightly above the consolute temperature of each system. The molal volumes were also measured over the limited composition range at two other temperatures 5° and 10° C. below the complete isotherm. For the systems perfluorocyclic oxide-n-heptane, perfluorocyclic oxide-carbon tetrachloride, and perfluoroheptane-n-heptane the isothermal volume measurements were made at 40°, 45°, and 50° C. while for the system perfluoroheptane-carbon tetra-

chloride they were made at 50°, 55°, and 60° C. The thermal coefficient of expansion of the materials limited the temperature range to ten degrees for one filling of the pycnometer.

Since some of the mixtures were two liquid phases at room temperature it was necessary to fill the pycnometer at a temperature above the consolute temperature. Figure 23 shows the arrangement for filling the pycnometer. The desired mixture was weighed out into the transfer tube, which was then closed off by means of a ground glass stopper and placed in the water bath at a temperature above the consolute temperature of the system. After remaining in the water bath several minutes the tube was shaken until mixing was complete and the ground glass stopper was replaced by the syphon tube, which had been heated to the bath temperature. The pycnometer was connected to the transfer tube by a small section of Tygon tubing and was filled by applying suction to the other arm. The pycnometer was always filled at the highest temperature of each series. The pycnometer reading was taken after approximately fifteen minutes at the bath temperature, then the bath temperature was lowered five degrees to the next temperature.

The water bath temperature was controlled manually

by means of an electrical heating element connected through a Variac. The mercury-in-glass thermometer measuring the bath temperature could be read to $\pm 0.02^\circ$ C. and was checked against a thermocouple calibrated by the National Bureau of Standards. The temperature of the bath never varied more than 0.05° C. from the desired temperature while the pycnometer was approaching thermal equilibrium. After the pycnometer reading was made at the three temperatures the pycnometer was removed from the bath and allowed to cool to room temperature. The pycnometer was then weighed, emptied, and weighed empty; all weights were corrected to weights in vacuo. Knowing the weight of material in the pycnometer, the composition of the material, and the pycnometer readings, it is a simple matter to find the molal volumes of the mixture at the three temperatures.

The molal volume-composition data is tabulated in Table XVI. The volume change on mixing was calculated by equation 17

$$\Delta V^M = V_M - x_1 V_1 - x_2 V_2 = V_M - V_0 \quad (17)$$

The partial molal volume change on mixing was determined by plotting the total volume change versus mole fraction of hydrocarbon, graphically taking the tangent to the curve at the desired composition, and determining the value of the

intercepts of the tangent line at $x_1 = 0$ and $x_1 = 1$. These values of the intercepts are the partial molal volume changes of mixing of components 2 and 1 respectively. Plots of the total volume change on mixing (ΔV^H) versus mole fraction of hydrocarbon are shown on Figures 24-27. Values of the partial molal volume changes on mixing are tabulated in Table XVII and plotted versus composition on Figures 28-31.

Figure 32 shows the plots of partial molal volume changes versus composition for the systems perfluorocyclic oxide-n-heptane and perfluoroheptane-n-heptane superimposed. One can see from Figure 32 that the partial molal volume changes are practically identical for each type of compound in both solutions and since the systems are almost symmetrical the partial molal volume changes are nearly equal for all three components. Since the two systems involving carbon-tetrachloride were not determined at the same temperature one would not expect the two partial molal volume change curves to be superimposed.

It was found for these four systems that the total volume change on mixing increased with increasing temperature; this type of behavior was also found in the C_5F_{12} - C_5H_{12} , C_4F_{10} - C_4H_{10} and C_6F_{14} - C_6H_{14} systems (2).

The coefficient of thermal expansion (α) as defined by equation 18 was determined from the temperature-volume data of the pure compounds and the binary mixtures.

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad (18)$$

Figures 33-36 show that plots of α versus composition for some of the systems exhibit maxima. The thermal coefficient of expansion for an ideal mixture (α_o) is a linear function of the volume fraction as shown below.

$$\begin{aligned} \alpha_o &= \frac{1}{x_1 V_1 + x_2 V_2} \frac{\partial}{\partial T} (x_1 V_1 + x_2 V_2)_P \\ \alpha_o &= \frac{x_1 V_1 \alpha_1 + x_2 V_2 \alpha_2}{x_1 V_1 + x_2 V_2} \\ \alpha_o &= \phi_1 \alpha_1 + \phi_2 \alpha_2 \end{aligned} \quad (19)$$

Equation 19 is also plotted on Figures 33-36 for comparative purposes. In order for the total volume change to increase with temperature it is necessary that the thermal coefficient of expansion for the mixture be greater than the coefficient for an ideal solution. This can be shown by differentiating equation 17 with respect to temperature

$$\frac{d \Delta V^M}{dT} = \frac{dV_M}{dT} - \frac{dV_o}{dT} = V_M \alpha_M - V_o \alpha_o$$

Since $V_M \approx V_0$

$$\frac{d \Delta V^M}{dT} = V_M(\alpha_M - \alpha_0)$$

In order for $\frac{d \Delta V^M}{dT}$ to be positive α_M must be greater than α_0 ; this is in accord with the experimental values of ΔV^M and α_M .

Since the values of α plotted on Figures 33-36 were determined in the region of the consolute temperature the large values of α might be due to the breaking up of clusters in the liquid as the temperature increases. The formation of clusters in systems exhibiting partial miscibility has been generally recognized (50). The opalescence observed just above the consolute temperature is believed due to the scattering of light by clusters of molecules.

A molecule in a cluster would have more like-molecules as nearest neighbors than it would have if the mixture were homogeneous; as the temperature is raised thermal motion combats the tendency to cluster and the mixture approaches homogeneity. If we consider the case where one 1-1 and one 2-2 pair rearrange to form two 1-2 pairs we find that the interaction energy of the system containing 1-2 pairs is $2\epsilon_{12}$ while the interaction energy of the system containing 1-1 and 2-2 pairs is $\epsilon_{11} + \epsilon_{22}$ or twice the arithmetic

mean of ϵ_{11} and ϵ_{22} . Since ϵ_{12} is approximately the geometric mean of ϵ_{11} and ϵ_{22} where only dispersion forces are acting, and since the geometric mean is always less than the arithmetic mean, the interaction energy of the system is less when 1-2 pairs are present. These weaker attractive forces result in a volume expansion and an increase in the enthalpy of the system.

The dispersion of clusters due to thermal agitation would explain the fact that the volume change on mixing increases with temperature and thus one would also expect the heat of mixing to increase with temperature. The heats of mixing in the system perfluoroheptane-iso-octane (26) were found to increase with temperature as shown by the following values; at a mole fraction of one-half, the heats of mixing were 402, 468, and 616 calories per mole at 30°, 50°, and 70° C. respectively. The volume change on mixing for this system was reported only at 30° C. However, the data of Taylor and Reed (42) show that the volume change on mixing for this system also increases with temperature.

The volume change on mixing is an important property in the study of solutions and for this reason it would be desirable to have a theoretical expression which would predict this property. Scatchard (38) and Hildebrand (13) have

shown that the Gibbs free energy at constant pressure (ΔF_p) is related to the Helmholtz free energy at constant volume (ΔA_v) by the following equation

$$\Delta F_p = \Delta A_v - \frac{1}{2\beta v} (\Delta v^H)^2 \quad (20)$$

The correction term involving Δv^H amounts to less than 10 calories per mole as compared to about 350 calories per mole for ΔF_p , and for this reason it is usually neglected. Hildebrand used this approximation in deriving an expression for the volume change on mixing. He started with the thermodynamic relation

$$\Delta v = \left(\frac{\partial \Delta F}{\partial p} \right)_T \quad (21)$$

and by substituting ΔA_v for ΔF_p he obtained

$$\Delta v = \left(\frac{\partial \Delta E_v}{\partial p} \right)_T - T \left(\frac{\partial \Delta S_v}{\partial p} \right)_T \quad (22)$$

By further assuming that the pressure derivative of the entropy was zero he arrived at

$$\Delta v = \left(\frac{\partial \Delta E_v}{\partial p} \right)_T = \left(\frac{\partial \Delta E_v}{\partial v_o} \right)_T \left(\frac{\partial v_o}{\partial p} \right)_T = -v_o \beta_o \left(\frac{\partial \Delta E_v}{\partial v_o} \right)_T \quad (23)$$

His final assumption was that

$$\left(\frac{\partial E}{\partial v} \right)_T = n \frac{\Delta E^v}{v} \quad (24)$$

and that $n = 1$.

This assumption is based on the fact that for several non-polar liquids the internal pressure, $\left(\frac{\partial E}{\partial V}\right)_T$, as calculated from the thermodynamic relation

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \quad (25)$$

can be represented by equation 24 where the coefficient n varies from 0.9 to 1.1. After making this assumption, Hildebrand arrived at the following equation for ΔV^M

$$\Delta V^M = \beta_0 \Delta E_V^M \quad (26)$$

Using equation 1 for ΔE_V^M yields

$$V^M = \beta_0 (x_1 V_1 + x_2 V_2) (\delta_1 - \delta_2)^2 \phi_1 \phi_2 \quad (27)$$

An alternate theoretical expression for ΔV^M can be obtained using Reed's (32) correction instead of the geometric mean assumption, but retaining the condition of constant volume.

Under these conditions ΔE_V^M is given by

$$\Delta E_V^M = (x_1 V_1 + x_2 V_2) \left[(\delta_1 - \delta_2)^2 + 2 \delta_1 \delta_2 (1 - f_I f_D) \right] \phi_1 \phi_2 \quad (28)$$

$$\text{where } f_I = \frac{2(I_1 I_2)^{1/2}}{I_1 + I_2} \quad (29)$$

$$f_D = \frac{2(d_{22}^0/d_{11}^0)^{1/2}}{1 + d_{22}^0/d_{11}^0} \quad (30)$$

The ratio d_{22}^0/d_{11}^0 can be evaluated from the cube root of

the molar volume ratio. Substituting equation 28 into equation 26 results in

$$\Delta V^M = \beta_0(x_1V_1 + x_2V_2) \left[(\delta_1 - \delta_2)^2 + 2\delta_1\delta_2(1 - f_I f_D) \right] \phi_1 \phi_2 \quad (31)$$

Still another expression can be obtained for ΔV^M if it is assumed that the entropy of mixing at constant volume is the ideal value, then ΔE_V^M in equation 26 can be replaced by ΔF_P^e according to the following:

$$\Delta F_P = \Delta A_V = \Delta E_V^M - T \Delta S_V$$

and

$$\Delta F_P^e = \Delta E_V^M - T \Delta S_V^e$$

If ΔS_V is assumed to have the ideal value then

$$\Delta S_V^e = 0$$

and

$$\Delta F_P^e = \Delta E_V^M$$

thus

$$\Delta V^M = \beta_0 \Delta F_P^e \quad (32)$$

In order to calculate ΔV^M from equations 27, 31, and 32, it is necessary to know β_0 , the compressibility of a solution showing no volume change on mixing. The compressibility is defined by equation 33

$$\beta = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad (33)$$

and it can be shown that β_0 is a linear function of the

volume fraction as was α_o .

$$\beta_o = \phi_1 \beta_1 + \phi_2 \beta_2 \quad (34)$$

Isothermal compressibility data needed for equations 34, 27, 31, and 32 are available in the literature for perfluoroheptane, and carbon tetrachloride (20) and n-heptane (46). Pressure-volume-temperature data for liquid isooctane are also available in the literature (3) from which the isothermal compressibility was determined by graphical differentiation. Westwater, Frantz, and Hildebrand (46) have shown that for a pure liquid the quantity a as defined by equation 35 is independent of temperature

$$a = v^2 T \alpha / \beta \quad (35)$$

Equation 35 can be used to extrapolate compressibility data from one temperature to another if volume and coefficient of thermal expansion data are also available. The values of β used in equation 34 are tabulated below in Table III.

TABLE III

ISOTHERMAL COMPRESSIBILITIES FOR USE IN EQUATION 34

Compound	Temperature °C.	β Atm^{-1}
C_7F_{16}	30	$2.65(10^{-4})$
C_7F_{16}	50	$3.03(10^{-4})$
C_7F_{16}	60	$3.42(10^{-4})$
$\text{n-C}_7\text{H}_{16}$	50	$1.82(10^{-4})$
CCl_4	60	$1.55(10^{-4})$
$\text{i-C}_8\text{H}_{18}$	30	$1.21(10^{-4})$

Values of Δv^M as calculated from equations 27, 31, and 32 are plotted on Figures 37-39 along with the experimental values for the systems perfluoroheptane-carbon tetrachloride, perfluoroheptane-n-heptane, and perfluoroheptane-iso-octane. Figure 37 reveals that for the $\text{C}_7\text{F}_{16}\text{-CCl}_4$ system the agreement between experimental values of Δv^M and those calculated from the experimental ΔF_p^e is quite good; the theoretical equation 31 also gives a fairly good estimate of Δv^M . For the systems $\text{C}_7\text{F}_{16}\text{-n-C}_7\text{H}_{16}$ and $\text{C}_7\text{F}_{16}\text{-i-C}_8\text{H}_{18}$, however, all these relations prove to be

poor estimates of Δv^M . It should also be noted that the theoretical equations 27 and 31 predict values of Δv^M which are symmetrical with respect to volume fraction and therefore should have their maximum values at a volume fraction of 0.5 (about 0.3 - 0.4 mole fraction of fluorocarbon). Figures 24-27 reveal that the volume changes for the four systems of this work and the C_7F_{16} - i - C_8H_{18} system are more nearly symmetrical with respect to mole fraction, having their maxima at a mole fraction of approximately 0.5.

Since equations 27, 31, and 32 failed to predict reasonable values for Δv^M it might be instructive to examine critically some of the assumptions and approximations involved in obtaining equation 26.

The first approximation involved the neglect of the pressure derivative of the correction term $\frac{(\Delta v^M)^2}{2\beta v}$ when substituting for ΔF_p^G in equation 21. Although this term is small and can be neglected in equation 20 its pressure derivative may not be small enough to be neglected in equation 22. Another source of error in equation 26 might result from the assumption that the pressure derivative of the entropy term in equation 22 is zero. It should be mentioned, however, that unless these two assumptions are made the expression for Δv^M becomes extremely complicated.

Another assumption, the effects of which can be clearly seen, is the assumption that the internal pressure can be represented by equation 24, where n is equal to unity. The data are available with which to calculate the internal pressure of perfluoroheptane (20) from equation 25. This calculation was made and it was found that a value of n equal to 1.40 was necessary to satisfy equation 24.

If the coefficient n is not assumed equal to unity, equation 26 would be written

$$\Delta V^M = n \beta_0 \Delta E_V^M \quad (36)$$

Since n for a fluorocarbon-hydrocarbon mixture would probably lie between 1.0 and 1.4, equation 36 would predict values of ΔV^M larger than those predicted by equations 27, 31, and 32, which implicitly assume a value of n equal to unity. A value of n between 1.0 and 1.4, however, would still predict low values of ΔV^M for the $C_7F_{16}-n-C_7H_{16}$ and $C_7F_{16}-i-C_8H_{18}$ systems since a value of n between 2.0 and 3.0 would be required for these systems. Since equations 31 and 32 closely predict ΔV^M for the $C_7F_{16}-CCl_4$ system the inclusion of n in equation 36 would impair the agreement in this case.

It is possible that equation 26 is reasonably correct and that the expressions for ΔE_v^M are in error. This possibility will be discussed in more detail in Chapter VII.

It is concluded that there are many assumptions and approximations involved in the derivation of equation 26 which prevent the accurate prediction of volume changes.

CHAPTER VII

ESTIMATION OF THERMODYNAMIC PROPERTIES

Heat of Mixing.---It was previously mentioned that Reed rederived the equations of Scatchard and Hildebrand omitting the assumptions of no volume change and the geometric mean, and obtained an expression which predicted heats of mixing in agreement with experimental values. Reed's expression for the heat of mixing in a binary mixture is given below:

$$\Delta E_P^M = (x_1 v_1 + x_2 v_2) \left[(\bar{\phi}_1 - \bar{\phi}_2)^2 - 2 \bar{\phi}_1 \bar{\phi}_2 (1 - f_I f_D) \right] \phi_1 \phi_2 + E_1^V (1 - \frac{v_1}{\bar{v}}) + E_2^V (1 - \frac{v_2}{\bar{v}}) \quad (37)$$

Where
$$\phi = \left(\frac{\Delta E^V}{\bar{v}^2} \right)^{1/2} = \left(\frac{v}{\bar{v}} \right) \phi \quad (38)$$

The terms f_I and f_D were defined previously by equations 29 and 30. Although equation 37 predicts values of ΔE_P^M it can be shown that the difference between ΔE_P^M and ΔH_P is negligible. In order to use equation 37 it is necessary to know the ionization potentials and partial molal volumes of components 1 and 2. Reed (34) has presented a method of predicting the ionization potential of a compound from its polarizability and structure which yields good results and can be used in the absence of experimental data.

Hildebrand (14) has shown that by considering the vol-

ume change on mixing that the heat of mixing can be calculated from the following expression.

$$\Delta H_P = \Delta E_V^M (1 + \alpha T) \quad (39)$$

If the entropy change at constant volume is assumed ideal, then ΔE_V^M can be replaced by ΔF_P^e and

$$\Delta H_P = \Delta F_P^e (1 + \alpha T) \quad (40)$$

Equation 40 can be used to calculate heats of mixing in fluorocarbon-hydrocarbon systems for which the thermal coefficient of expansion (α) is known and where ΔF_P^e can be calculated from the binary solubility data as outlined in Chapter V.

Still another method of estimating the heat of mixing involves the use of the following thermodynamic relation

$$\Delta H_P = \Delta F_P + T \Delta S_P \quad (41)$$

In terms of the excess properties, equation 41 can be written

$$\Delta H_P = \Delta F_P^e + T \Delta S_P^e \quad (42)$$

Since a method of estimating ΔF_P^e is available it is only necessary to estimate ΔS_P^e . The entropy change due to the volume change on mixing can be determined from the following Maxwell relation

$$\left(\frac{\partial S}{\partial V} \right)_P = \left(\frac{\partial P}{\partial T} \right)_V \quad (43)$$

For a volume change at constant pressure ΔS is given by

$$\Delta S = \int_{V_0}^{V_0 + \Delta V^M} \left(\frac{\partial P}{\partial T} \right)_V dV \quad (44)$$

By assuming that $\left(\frac{\partial P}{\partial T}\right)_V$ is constant over the small volume change, equation 44 results in

$$\Delta S = \left(\frac{\partial P}{\partial T}\right)_V \Delta V^M \quad (45)$$

The ΔS in equation 45 represents the change in entropy between a constant pressure and a constant volume process. Equation 45 can then be used in equation 42 giving

$$\Delta H_P = \Delta F_P^e + T \left(\frac{\partial P}{\partial T}\right)_V \Delta V^M + T \Delta S_V^e \quad (46)$$

If ΔS_V^e is again assumed equal to zero, equation 46 can be used to calculate heats of mixing where binary solubility data, volume change on mixing data, and the value of $\left(\frac{\partial P}{\partial T}\right)_V$ for the pure compounds are available.

Westwater, Frantz, and Hildebrand have measured the quantity $\left(\frac{\partial P}{\partial T}\right)_V$ for several pure compounds and equimolar binary mixtures and have found that the $\left(\frac{\partial P}{\partial T}\right)_V$ term for mixtures can be calculated from those of the pure compounds through the following relation

$$a_{\text{mix}} = (x_1 a_1^{1/2} + x_2 a_2^{1/2})^2 \quad (47)$$

where a is defined by equation 35.

The heats of mixing have been calculated from equations 37, 40, and 46 for the systems C_7F_{16} - n - C_7H_{16} , C_7F_{16} - CCl_4 , C_7F_{16} - i - C_8H_{18} , C_5F_{12} - C_5H_{12} and C_4F_{10} - C_4H_{10} , and are plotted versus composition on Figures 49-53. The data necessary for these calculations is tabulated in Table XXVII.

The necessary $\left(\frac{\partial P}{\partial T}\right)_V$ data are not available for the

C_5F_{12} - C_5H_{12} and C_4F_{10} - C_4H_{10} systems and therefore equation 46 cannot be used. Figures 51-53 reveal that equations 37 and 40 predict values of the heat of mixing in good agreement with the reported literature values. The agreement between equations 37, 40, and 46 is very good in the case of the C_7F_{16} - CCl_4 system although no experimental values of ΔH_p are available for comparison. Agreement between equations 37, 40, and 46 is not too good, however, in the C_7F_{16} - n - C_7H_{16} system where again no experimental values of ΔH are available for comparison.

Free Energy of Mixing.--As was mentioned in Chapter V the excess free energy of mixing can be estimated quite well from binary solubility data. Equation 28 can also be used to estimate excess free energy of mixing if it is assumed that the entropy of mixing at constant volume has the same value as for an ideal system. Figures 18-20 show a comparison of ΔF_p^e calculated from equation 28 and from binary solubility data. Reported literature values of ΔF_p^e are available for comparison in the C_5F_{12} - C_5H_{12} , C_4F_{10} - C_4H_{10} , and C_7F_{16} - i - C_8H_{18} systems. In the case of C_7F_{16} - CCl_4 no literature values are available, but agreement between ΔF_p^e calculated from equation 28 and ΔF_p^e calculated from solubility data is good. In the remaining systems equation 28 always predicts values of ΔF_p^e which are too low.

The excess free energy of mixing can be estimated in an empirical manner. If it is assumed that equation 28 is

the correct expression for ΔE_V^M and that the excess entropy of mixing at constant volume can be represented by equation 48, then it is possible to write equation 49 for ΔF_P^e .

$$\Delta S_V^e = -z(x_1V_1 + x_2V_2) \left[(\sigma_1 - \sigma_2)^2 + 2\sigma_1\sigma_2(1 - f_I f_D) \right] \phi_1 \phi_2 \quad (48)$$

$$\Delta F_P^e = (1 + zT)(x_1V_1 + x_2V_2) \left[(\sigma_1 - \sigma_2)^2 + 2\sigma_1\sigma_2(1 - f_I f_D) \right] \phi_1 \phi_2 \quad (49)$$

The term z in equation 49 is merely a correction factor and can be determined from an empirical correlation of z versus $\left[(\sigma_1 - \sigma_2)^2 + 2\sigma_1\sigma_2(1 - f_I f_D) \right]$ shown on Figure 55.

Values of z used in establishing this correlation were obtained from free energy and consolute temperature data reported in the literature for fifteen fluorocarbon-hydrocarbon systems. For all these systems the equations of Scatchard and Hildebrand predict values of the free energy or consolute temperature which are too low.

The Scatchard-Hildebrand equations for the excess free energy and consolute temperature can be written

$$\Delta F^e = (x_1V_1 + x_2V_2)K \phi_1 \phi_2 \quad (50)$$

$$RT_C = \frac{2x_1x_2V_1^2V_2^2K}{(x_1V_1 + x_2V_2)^3} \quad (51)$$

$$\text{where } K = (1 + zT) \left[(\sigma_1 - \sigma_2)^2 + 2\sigma_1\sigma_2(1 - f_I f_D) \right] \quad (52)$$

The parameter K represents the effective value of

$$\left[(\sigma_1 - \sigma_2)^2 + 2\sigma_1\sigma_2(1 - f_I f_D) \right]$$

necessary to fit the Scatchard-Hildebrand equations to the

experimental data. The value of z was determined from the reported free energy and consolute temperature data by using equations 50, 51, and 52. Values of K and z for the fifteen systems are tabulated in Table XXVIII along with the literature reference and the method of obtaining K .

This correlation is only applicable to mixtures of fluorocarbons and paraffin hydrocarbons. Systems containing benzene, carbon tetrachloride and chloroform could not be so correlated. A glance at Figure 55 reveals that the points are widely scattered about the correlation line and suggests that values of ΔF_p^e calculated from z and equation 49 would be subject to quite a bit of error. This is not the case because z is a correction factor and large differences in z result in smaller differences in the factor $1 + zT$. This correlation fits the excess free energy data with an average deviation of 7 per cent and a maximum deviation of 20 per cent.

Entropy of Mixing.—The entropy of mixing at constant pressure can be given by equation 45

$$\Delta S_p = \Delta S_v + \left(\frac{\partial P}{\partial T} \right)_v \Delta V^M \quad (45)$$

or in terms of the excess properties

$$\Delta S_p^e = \Delta S_v^e + \left(\frac{\partial P}{\partial T} \right)_v \Delta V^M \quad (45)$$

For the $C_7F_{16}-i-C_8H_{18}$ system values of ΔS_p^e and ΔV^M have been reported (26) and the necessary $\left(\frac{\partial P}{\partial T}\right)_V$ data are available in the literature (20) (3). Values of $T\Delta S_p^e$ and $T\left(\frac{\partial P}{\partial T}\right)_V \Delta V^M$ are plotted versus composition on Figure 56 where it can be seen that the $T\left(\frac{\partial P}{\partial T}\right)_V \Delta V^M$ term is much larger than $T\Delta S_p^e$ indicating negative values for ΔS_v^e . Negative values of ΔS_v^e would also explain the fact that ΔF^e as calculated from equation 28 are lower than experimental values, since in using equation 28, ΔS_v^e was assumed equal to zero. These negative values of ΔS_v^e would also explain the large difference between experimental values of ΔH and those calculated by equation 46 as shown on Figure 51. The same conclusion concerning ΔS_v^e in the $C_7F_{16}-n-C_7H_{16}$ system could also be drawn from Figure 49.

The $C_7F_{16}-CCl_4$ system, however, appears to have a value of ΔS_v^e equal to zero since from Figure 54 it can be seen that ΔF^e calculated from equation 28 is in agreement with ΔF^e determined from solubility data. Also values of ΔH calculated from equations 37, 40, and 46 are in good agreement as shown on Figure 50.

Another argument in favor of negative values of ΔS_v^e is the fact that the empirical correlation involving

z and equation 49 predicts free energies of mixing. This correlation is based on the assumption that ΔS_V^e can be predicted by equation 43. Since z is a positive number then ΔS_V^e as given by equation 43 will be negative.

If negative values of ΔS_V^e are common to most fluorocarbon-hydrocarbon solutions, it is surprising that equation 40 predicts values of ΔH in agreement with experimental values in the C_7F_{16} - C_8H_{18} , C_5F_{12} - C_5H_{12} , and C_4F_{10} - C_4H_{10} systems. In order to understand why equation 40 is successful in this respect it would be well to examine its derivation. This is done in the following paragraphs.

In order to determine the effect of small volume changes on ΔE_V^M as given by equation 1, Hildebrand expanded ΔE_V^M about V_0 using a Taylor series and obtained

$$\Delta E_P^M = \Delta E_V^M + \left(\frac{\partial \Delta E^M}{\partial V} \right)_T \Delta V^M + \left(\frac{\partial^2 \Delta E^M}{\partial V^2} \right)_T \frac{(\Delta V^M)^2}{2} + \dots \quad (53)$$

By neglecting second order and higher terms in ΔV^M and using the thermodynamic relation

$$\left(\frac{\partial \Delta E}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V - P$$

he obtained

$$\Delta E_P^M = \Delta E_V^M + T \left(\frac{\partial P}{\partial T} \right)_V \Delta V^M - P \Delta V^M \quad (54)$$

The relation between ΔE_P^M and ΔH_P is

$$\Delta H_P = \Delta E_P^M + P \Delta V^M \quad (55)$$

Substituting equation 55 into equation 54 gives

$$\Delta H_P = \Delta E_V^M + T \left(\frac{\partial P}{\partial T} \right)_V \Delta V^M \quad (56)$$

We have already seen from equation 26 that the volume change on mixing is related to the energy of mixing at constant volume

$$\Delta V^M = \beta_0 \Delta E_V^M \quad (26)$$

By substituting equation 26 into equation 56 Hildebrand obtained

$$\Delta H_P = \Delta E_V^M + T \frac{\alpha}{\beta} \beta_0 \Delta E_V^M \quad (57)$$

If β and β_0 are assumed equal then equation 39 results

$$\Delta H_P = \Delta E_V^M (1 + \alpha T) \quad (39)$$

A possible reason why equation 40 predicts reasonable values of ΔH in spite of negative values of ΔS_V^e is apparent from equation 56. The substitution of ΔF^e for

ΔE_V in equation 56 would result in values of ΔH which were too high. This effect is compensated by expressing ΔV^M by equation 26, which we have seen generally predicts values of ΔV^M which are too low. Thus equation 40 provides a good estimate of ΔH , probably due to a fortuitous cancellation of errors.

The fact that it is possible for equation 40 to predict reasonable values for ΔH even though ΔS_V^e is not zero

and the fact that ΔF^e as calculated by equation 28 is less than the observed values leads to the conclusion that ΔS_V^e could also be negative in the C_5F_{12} - C_5H_{12} and C_4F_{10} - C_4H_{10} systems.

Negative values of ΔS_V^e for fluorocarbon-hydrocarbon systems are not unreasonable and are consistent with the concept of clustering. In a mixture containing clusters, the distribution of molecules would not be random and one would expect the entropy of mixing to be less than the ideal value. The effect of raising the temperature would be to increase the random thermal motion of the molecules and decrease the clustering tendency. Thus the value of ΔS_V^e should become less negative as the temperature is increased, causing the value of ΔS_P^e to increase with temperature. This effect was found in the C_7H_{16} - i - C_8H_{18} system where the following values of ΔS_P^e were reported for an equimolar mixture.

t	ΔS_P^e (cal./mole $^{\circ}K.$)
30 $^{\circ}C.$	0.24
50 $^{\circ}C.$	0.46
70 $^{\circ}C.$	0.89

CHAPTER VIII

TERNARY LIQUID--LIQUID SOLUBILITY STUDIES

The ternary liquid-liquid solubility studies were undertaken to determine whether fluorocarbon mixtures could be separated by solvent extraction, and whether fluorocarbons would be good solvents for mixtures of other types of compounds. Various types of organic compounds were tested as possible solvents for separating a mixture of perfluoroheptane (C_7F_{16}) and perfluorocyclic oxide ($C_8F_{16}O$).

Experimental.--These preliminary studies were performed by vigorously shaking an approximately equimolar mixture of the two fluorocarbons with the prospective solvent in a small screw-cap vial and using a Perkin-Elmer "Vapor Fractometer" to analyze the two coexisting liquid phases. The criterion of a good prospective solvent was taken to be the difference in the C_7F_{16} and $C_8F_{16}O$ peak height fractions in the two liquid phases. Of all the organic solvents tested, carbon tetrachloride (CCl_4) and *n*-heptane ($n-C_7H_{16}$) were found to be the most promising. The ternary liquid-liquid phase diagrams were determined for the systems C_7F_{16} - $C_8F_{16}O$ - $n-C_7H_{16}$ and C_7F_{16} - $C_8F_{16}O$ - CCl_4 at 30° C.

The methyl ester of perfluoro-octanoic acid ($\text{C}_7\text{F}_{15}\text{COOCH}_3$) was tested as a possible solvent for mixtures of toluene ($\text{C}_6\text{H}_5\text{CH}_3$) and methyl cyclohexane ($\text{C}_6\text{H}_{11}\text{CH}_3$) since the consolute temperatures for these two binary systems containing the ester were quite different. Toluene and the ester are completely miscible at room temperature whereas the consolute temperature of the methylcyclohexane-ester system is 45°C . The ternary liquid phase diagram was determined for this system at 25° and 10°C .

The isothermal ternary liquid phase diagrams were determined from chromatographic analysis of the two coexisting liquid phases. The liquid mixture was contained in a screw-cap vial and was vigorously shaken while immersed in a water bath. After being shaken for some time, samples of each phase consisting of approximately 0.04 ml. were withdrawn for analysis by a hypodermic syringe and the mixture was again shaken. Two or three successive samples were taken with shaking in between sampling. The hypodermic syringe was warmed to approximately 10°C . above the temperature of the mixture prior to sampling in order to prevent any concentration changes due to cooling the saturated phases. The sample was injected into the chromatograph immediately after sampling so as to prevent formation of a second phase in the syringe upon cooling.

The water bath used in these determinations was described in Chapter VI. The vial was shaken by hand during the determination of the toluene-methylcyclohexane-ester system, but it was found that considerable shaking was necessary to effect equilibrium between phases in the two perfluoroheptane-perfluorocyclic oxide systems. Therefore, the vial was shaken by an air-driven mechanism for approximately thirty minutes before and between sampling. The agreement between the analyses for successive samples was taken as the criterion of equilibrium.

Since analyses were performed chromatographically, it was first necessary to find a suitable partitioning liquid that would resolve the ternary mixture into three separate peaks on the chromatograph with no overlapping. After the proper partitioning liquid had been found, it was then necessary to prepare calibration curves of peak height fraction against weight fraction for two of the three possible binary mixtures, since it was found that a ternary mixture could be analyzed from calibration data for only two of the three possible binary mixtures. This is due to the fact that the solutes are in very low concentration in the partitioning liquid and therefore act independently of each other. The calibration data and curves used for analyses are given in Tables XVIII and Figures 40-44.

The peak height fraction for successive samples of one phase were usually in good agreement and the composition was determined from the average peak height fractions. Where significant differences occurred between peak height fractions of successive samples, the compositions of each sample were also calculated and are tabulated. The tie line data necessary for construction of the phase diagrams is tabulated in Table XIX and the phase diagrams are shown on Figures 45-48.

Conjugate curves are drawn on the phase diagrams for the purpose of interpolating tie lines; the plait points for two of the systems were estimated by extrapolating the conjugate curve to its intersection with the binodal curve. These conjugate curves were constructed from points located by drawing lines through each end of the tie lines parallel to the sides of the diagram in such a manner that these two lines intersected inside the diagrams.

Varteressian and Fenske (44) found that ternary solubility data could be represented by the following relationship

$$\beta = \frac{w_1}{w_1'} \cdot \frac{w_2'}{w_2} = \frac{x_1}{x_1'} \cdot \frac{x_2'}{x_2}$$

The term β is known as the selectivity of the solvent and gives a measure of the ease with which a binary mixture can be separated with a given solvent by solvent extraction

methods. A β value of unity would indicate no selectivity while solvents having higher values of β are more selective. The selectivity is analogous to the relative volatility which is used as a measure of the ease with which a binary mixture can be separated by distillation.

Values of the selectivity have been calculated from the tie line data and equation 58 for the four systems studied in this work. Since these values of the selectivity vary only slightly with composition, their average values are tabulated below in Table IV.

TABLE IV
SOLVENT SELECTIVITIES

<u>Mixture to be Separated</u>	<u>Solvent</u>	<u>t (°C.)</u>	β <u>Average</u>
$C_8F_{16}O-C_7F_{16}$	CCl_4	30°	1.20
$C_8F_{16}O-C_7F_{16}$	nC_7H_{16}	30°	1.09
$C_6H_5CH_3-C_6H_{11}CH_3$	$C_7F_{15}COOCH_3$	25°	1.16
$C_6H_5CH_3-C_6H_{11}CH_3$	$C_7F_{15}COOCH_3$	10°	1.23

Table IV shows that neither n-heptane nor carbon tetrachloride is a good solvent for the fluorocarbon mixture,

but that carbon tetrachloride is the better of the two. It is also obvious that the ester is not a good solvent for the hydrocarbon mixture.

From consideration of the Scatchard-Hildebrand theory one would not expect a nonpolar solvent to be very selective for either C_7F_{16} or $C_8F_{16}O$ since their solubility parameters (δ) are almost equal, being 5.93 and 6.05 respectively. The δ difference is a measure of the deviation of a binary system from Raoult's law as shown by equation 3. One can see that for a given solvent the δ difference between C_7F_{16} and solvent is practically the same as the δ difference between $C_8F_{16}O$ and solvent. The high solvent selectivity found in some reported systems can be attributed to specific effects such as association, solvation, or hydrogen bonding, which are not present in nonpolar systems. Since the solubility parameters of the fluorocarbons are almost equal, and since they are nonpolar they cannot exhibit specific interaction effects with the solvent. It is considered unlikely that a separation can be effected by solvent extraction.

Theoretical Calculation of Activities in Ternary Systems.—Hildebrand (15) has extended the treatment of solutions of nonelectrolytes to ternary systems and has arrived

at equations 59 for the activity coefficients in terms of the properties of the pure compounds.

$$RT \ln \gamma_1 = V_1 \left[(\delta_1 - \delta_2) \phi_2 + (\delta_1 - \delta_3) \phi_3 \right]^2 \quad (59)$$

$$RT \ln \gamma_2 = V_2 \left[(\delta_2 - \delta_1) \phi_1 + (\delta_2 - \delta_3) \phi_3 \right]^2$$

$$RT \ln \gamma_3 = V_3 \left[(\delta_3 - \delta_1) \phi_1 + (\delta_3 - \delta_2) \phi_2 \right]^2$$

Using equations 59 the activities in the two conjugate liquid phases can be calculated from the tie line data. If equations 59 correctly predict activity coefficients, the calculated activities must satisfy the condition that the activity of each component be equal in both phases.

$$x_1 \gamma_1 = x_1' \gamma_1'$$

$$x_2 \gamma_2 = x_2' \gamma_2' \quad (60)$$

$$x_3 \gamma_3 = x_3' \gamma_3'$$

Equations 59 were used along with the tie line data to calculate activities in the coexisting phases for the systems $C_7F_{16}-C_8F_{16}O-CCl_4$ and $C_7F_{16}-C_8F_{16}O-n-C_7H_{16}$. The solubility parameters were evaluated from the properties of the pure components. These calculated activity values are tabulated in Table XX. From Table XX it is obvious that the results of equations 59 do not satisfy the conditions of equations 60. If, however, equations 59 are used with the

solubility parameters evaluated from the binary solubility data, the activities are found to satisfy equations 60, as can be seen from Table XX.

The "effective" solubility parameters can be found from the binary solubility data by substituting equations 3 into equations 11 and 12. Two empirical values of each difference are obtained from this procedure since there are two equations (11 and 12) and only one unknown (the δ difference). It was found that there was only a slight difference between the two δ difference terms and therefore an average value was used for substitution into equation 59. Since the following relation holds

$$\delta_1 - \delta_2 = (\delta_1 - \delta_3) - (\delta_2 - \delta_3)$$

only the δ difference for two of the binary systems is needed to evaluate all possible δ differences required by equations 59. Values of the δ difference evaluated from the binary solubility data are compared with those evaluated from properties of the pure compounds in Table V.

TABLE V

COMPARISON OF δ DIFFERENCE

System	δ Difference	
	Pure Compounds	Solubility
$C_7F_{16}-n-C_7H_{16}$	1.43	2.87
$C_8F_{16}O-n-C_7H_{16}$	1.31	2.78
$C_7F_{16}-CCl_4$	2.52	3.10
$C_8F_{16}O-CCl_4$	2.40	2.94

Since the Van Laar equation has proved useful in treating binary systems it would be interesting to see if ternary systems are also amenable to this treatment. White (47) has applied the Van Laar equation to calculate equilibrium vapor-liquid compositions in ternary systems from data obtained from the binary systems. He compared the calculated results with experimental data for three ternary systems and found the agreement to be good enough for engineering purposes. Robinson and Gilliland (36) have shown that the Van Laar treatment can be extended to ternary systems where the Van Laar constants for only two binary systems are needed to calculate activity coefficients in the ternary system. The ternary Van Laar relations are

$$\begin{aligned}
 \ln \gamma_1 &= \left[\frac{x_2 \sqrt{A_{12}} + x_3 A_{32} \sqrt{A_{13}/B_{32}}}{x_1 A_{12}/B_{12} + x_2 + x_3 A_{32}/B_{32}} \right]^2 \\
 \ln \gamma_2 &= \left[\frac{x_2 A_{12} \sqrt{A_{21}} + x_3 A_{32} \sqrt{A_{23}/B_{32}}}{x_1 A_{12}/B_{12} + x_2 + x_3 A_{32}/B_{32}} \right]^2 \\
 \ln \gamma_3 &= \left[\frac{x_1 A_{12} \sqrt{A_{31}/B_{12}} + x_2 \sqrt{A_{32}}}{x_1 A_{12}/B_{12} + x_2 + x_3 A_{32}/B_{32}} \right]^2
 \end{aligned} \tag{61}$$

In evaluating the constants in equations 61 the following relations are used

$$\frac{A_{12}}{B_{12}} = \frac{B_{21}}{A_{21}}$$

and

$$A_{21} = B_{12}$$

Since the square roots of the binary Van Laar constants are needed for equations 61 the question arises as to whether the positive or negative root should be used. In This case the binary Van Laar equation is considered similar in form to equations 3, where the constants can be written

$$A_{12} = \frac{V_1}{RT} (\sigma_1 - \sigma_2)^2$$

$$B_{12} = \frac{V_2}{RT} (\sigma_2 - \sigma_1)^2$$

and

$$\frac{A_{12}}{B_{12}} = \frac{V_1}{V_2}$$

The square root of A_{12} is taken to be positive if σ_1 is

greater than σ_2 and negative if the reverse is true. The relation existing between the constants which allows the evaluation of all constants from the constants of two binary systems is

$$\sqrt{A_{12}} - \sqrt{A_{13}} + \sqrt{A_{23}} \sqrt{\frac{A_{12}}{B_{12}}} = 0$$

The necessary constants for use in equations 61 were determined from the binary Van Laar constants by the procedure described above. The activities for each component in the two coexisting phases were calculated for the systems $C_7F_{16}-C_8F_{16}O-CCl_4$ and $C_7F_{16}-C_8F_{16}O-n-C_7H_{16}$. These activities are tabulated in Table XXI and it can be seen that equations 61 satisfy the conditions of equations 60. Thus we see that equations 59 or 61 can be used to predict activities in ternary systems when the constants are evaluated experimentally from two binary systems.

It is also possible to use equations 59 or 61 to construct the ternary phase diagram from the binary solubility data. This can be done graphically by using equation 59 or 61 to plot contours of constant activity for each component on a triangular diagram. The composition of the two phases in equilibrium can be found by locating two points at which the activity of each component is equal. An attempt was made to use this method to calculate the phase

diagram for the $C_7F_{16}-C_8F_{16}O-CCl_4$ system, but location of the phase compositions proved very difficult since it was necessary to interpolate between three sets of activity contours.

CHAPTER IX

EXTRACTIVE DISTILLATION STUDIES

The term extractive distillation refers to the process of adding a solvent to a mixture to be separated by distillation in order to improve the relative volatility. The solvent is able to improve the relative volatility by altering the activity coefficients of the various components. The relative volatility (α) is defined for a binary mixture by equation 62

$$\alpha = \frac{y_1}{x_1} \cdot \frac{x_2}{y_2} \quad (62)$$

(In equation 62 the subscript 1 refers to the more volatile compound.) For systems obeying Dalton's law of partial pressures and where deviations from ideal gas behavior can be neglected the ratio y_1/x_1 is given by

$$y_1/x_1 = \frac{p_1^0 \gamma_1}{P}$$

Substituting into equation 62 gives

$$\alpha = \frac{p_1^0 \gamma_1}{p_2^0 \gamma_2} \quad (63)$$

From equation 63 it can be seen that by selecting a solvent

which increases the ratio of activity coefficients the relative volatility is increased.

In practice the solvent used is essentially non-volatile or of a low volatility compared to the original components and the quantity used is such that the original components are in low concentrations in the liquid phase and do not interact with each other appreciably. This being the case, the ternary mixture can be treated approximately as two binary mixtures involving each original component with the solvent. Since the solvent is essentially nonvolatile the vapor phase is assumed to consist only of the original components.

The Scatchard-Hildebrand theory can be used to predict some properties of a good solvent for extractive distillation. Assuming two independent binary systems, the expression for the logarithm of the activity coefficient ratio as given by equation 3 is

$$RT \ln \gamma_1 / \gamma_2 = V_1 (\delta_3 - \delta_1)^2 \phi_3^2 - V_2 (\delta_3 - \delta_2)^2 \phi_3^2 \quad (64)$$

(In equation 64 the subscript 3 refers to the solvent.)

If the molal volumes of components 1 and 2 are approximately equal then equation 64 becomes

$$\frac{2RT}{V_1 + V_2} \ln \gamma_1 / \gamma_2 = \left[2(\delta_2 - \delta_1) \delta_3 - (\delta_2^2 - \delta_1^2) \right] \phi_3^2 \quad (65)$$

From equation 65 we see that the logarithm of the activity coefficient ratio depends upon the square of the volume fraction of solvent and upon the solubility parameter of the solvent. From the standpoint of separating power the properties of a good solvent will be those which increase the right hand side of equation 64 or 65. This indicates that the molal volume and the solubility parameter are important factors in selecting a solvent. It is difficult to predict the effect of temperature upon the activity coefficient ratio as given by equation 65 since the molal volume changes in the same direction as the temperature, and the difference term is more or less independent of temperature. One would therefore not expect the activity coefficient ratio to be a strong function of temperature.

In this work several compounds will be evaluated as extractive distillation solvents for mixtures of perfluoroheptane (C_7F_{16}) and perfluorocyclic oxide ($C_8F_{16}O$); also n-heptane (n- C_7H_{16}) and methylcyclohexane ($C_6H_{11}CH_3$).

A convenient method of evaluating prospective extractive distillation solvents is by means of gas-liquid partition chromatography. Porter, Deal, and Stross (30) have shown that the activity coefficient of a solute in an infinitely dilute solution in the partitioning liquid can be obtained from the appearance time of the solute peak. The

activity coefficient ratio in equation 63 can be found from the appearance times of components 1 and 2 when the prospective solvent is used as the partitioning liquid. The following relations were given by Porter et al for determining the activity coefficient in the infinitely dilute solution.

$$V_R^0 = V_G + HV_S \quad (66)$$

$$H = RT / \gamma^0 p^0 \tilde{V}_S \quad (67)$$

$$V_R^0 = V_R / \left[\frac{2(p_1/p_0)^3 - 1}{3(p_1/p_0)^2 - 1} \right] \quad (68)$$

The volume occupied by the vapor phase in the column (V_G) is usually small compared to V_R^0 and can be neglected. Neglecting V_G and combining equations 66 and 67 we get

$$V_R^0 = \frac{V_S RT}{\gamma^0 p^0 \tilde{V}_S} \quad (69)$$

If the appearance times, Θ , for components 1 and 2 are determined under the same conditions of constant flow rate and constant pressure drop through the partitioning column then we can write

$$\frac{V_{R2}^0}{V_{R1}^0} = \frac{V_{R2}}{V_{R1}} = \frac{\Theta_2}{\Theta_1} \quad (70)$$

From equation 69 the ratio V_{R2}^0 / V_{R1}^0 can be written

$$\frac{V_{R2}^0}{V_{R1}^0} = \frac{\gamma_1^0 p_1^0}{\gamma_2^0 p_2^0} \quad (71)$$

Equating equations 70 and 71 gives

$$\frac{\gamma_1^0}{\gamma_2^0} = \frac{\Theta_2 p_2^0}{\Theta_1 p_1^0} \quad (72)$$

Substituting equation 72 into equation 63 yields the following expression for the relative volatility of components 1 and 2 at infinite dilution in the partitioning liquid.

$$\alpha = \Theta_2 / \Theta_1 \quad (73)$$

Since the value of the relative volatility as given by equation 73 is for an infinitely dilute solution, the ratio of the appearance times gives the maximum separation that can be obtained when using the partitioning liquid as an extractive distillation solvent.

Experimental.—The chromatography columns used in this work were made from one meter lengths of one-fourth inch copper tubing; these columns were used in a Perkin-Elmer "Vapor Fractometer," model 154.

The stationary phase was Celite C44857 (Johns-Manville), a diatomaceous earth having rather uniform particle size. Before this celite was used the very small particles were removed by allowing the material to settle in water and decanting the water containing the suspended fines. After this the celite was washed several times with concentrated hydrochloric acid, then washed with distilled water and dried

in an oven.

The prospective solvents were perfluorokerosene, and three Kel-F oils having the general structure $\text{Cl}(\text{CF}_2\text{CFCl})_x\text{Cl}$. These oils are products of the M. W. Kellogg Company and were designated Kel-F oils 1, 3, and 10. The M. W. Kellogg Company reports the following vapor pressures for these oils at 100° C.

Kel-F Oil 1...17 mm

Kel-F Oil 2... 1 mm

Kel-F Oil 10..0.1 mm

These four liquids were chosen as partitioning liquids since their vapor pressures were low enough to prevent their removal from the packing during operation of the column at adequate gas flow rates and temperatures. The ratio of partitioning liquid to Celite used in the preparation of the partitioning columns was 0.5 to 0.7 ml of liquid per gram of Celite. The weight of packing required to fill the column was measured so that the void volume and the volume of the stationary phase could be computed. The properties of these columns are tabulated in Table XXII.

The four above mentioned partitioning liquids were evaluated as possible extractive distillation solvents for the binary systems C_7F_{16} with $\text{C}_8\text{F}_{16}\text{O}$, and C_7H_{16} with $\text{C}_8\text{H}_{11}\text{CH}_3$.

Table XXIII gives the appearance times of C_7F_{16} , $C_8F_{16}O$, C_7H_{16} and $C_6H_{11}CH_3$ in the partitioning liquids and Table XXIV gives the values of the relative volatility as calculated from equation 73.

From Table XXIV it can be seen that all four solvents can be rated equally as extractive distillation solvents for both binary systems. The pronounced effect of temperature upon the relative volatility is also noted from Table XXIV.

The C_7F_{16} - $C_8F_{16}O$ system was investigated by Yen (49) and was found to obey Raoult's law. Since this system is ideal the relative volatility is merely the ratio of vapor pressures. Using the vapor pressures listed in the appendix for C_7F_{16} and $C_8F_{16}O$, the calculated relative volatilities for this system at 35° and 80° C. are 2.34 and 1.96 relatively. Using an average value of the relative volatility for these compounds in the four solvents it can be seen that the addition of the solvent changed the relative volatility from 2.34 to 2.62 at 35° C. and from 1.96 to 2.16 at 80° C. This change corresponds to a change in V_1/V_2 from 1.00 to 1.11 at 35° C. and from 1.00 to 1.10 at 80° C. The effect of temperature upon the activity coefficient ratio is very slight as was previously suggested.

The n-heptane-methylcyclohexane system was investigated by Bromiley and Quiggle (4), who found the average value of the relative volatility to be 1.074 in the temperature range 90° to 101° C. The system obeys Raoult's law and the relative volatility can be expressed as the ratio of vapor pressures. Using the vapor pressures calculated from the Antoine equation given by reference 1 the calculated relative volatilities for this system are 1.003 and 1.057 at 35° and 80° C. respectively.

Again using the average value of the relative volatility for all solvents it is seen that the relative volatility for these hydrocarbons changed from 1.003 to 1.11 at 35° and from 1.057 to 1.21 at 80° C. The addition of the solvent caused the activity coefficient ratio to change from 1.00 to 1.11 at 35° C. and from 1.00 to 1.14 at 80° C. Again the effect of temperature on the activity coefficient ratio is seen to be slight.

Since the physical properties necessary for evaluation of the solubility parameters of the solvents (δ_3) are not available it is not possible to predict the expected value of the activity coefficient ratio as given by equation 64 or 65. Equation 64 can be used, however, to evaluate the solvent solubility parameter (δ_3) by using the experimentally determined activity coefficient ratio and the necessary phys-

ical properties of the solutes given in Table XXVI. Values of δ_3 were calculated from data for the $C_7F_{16}-C_8F_{16}O$ - solvent, and $C_7H_{16}-C_6H_{11}CH_3$ - solvent systems at the temperatures of 35° C. and 80° C. These values of δ_3 are tabulated below and it can be seen that δ_3 has essentially the same value when evaluated from experimental data from two different systems.

TABLE VI
CALCULATION OF δ_3 FROM EQUATION 64

t(°C.)	$C_7F_{16}-C_8F_{16}O$ -Solvent	$C_7H_{16}-C_6H_{11}CH_3$ -Solvent
35	7.88	8.05
80	7.50	7.52

The results in Table VI indicate that the equations of Scatchard and Hildebrand are applicable to prediction of solvent properties. From the results of Table VI the average solvent solubility parameters are 7.96 at 35° C. and 7.51 at 80° C.

These values of the solubility parameter may seem somewhat high for chlorofluorocarbon compounds since chlorofluorocarbons for which data are available have solubility parameters between those of fluorocarbons and hydrocarbons

having the same boiling points. It should be noted, however, that the solubility parameter increases with increasing molecular weight within a homologous series as is obvious from the following table of solubility parameters for the paraffin series as reported by Hildebrand (16).

<u>compound</u>	<u>δ at 25° C.</u>
<u>n-C₅H₁₂</u>	7.05
<u>n-C₆H₁₄</u>	7.30
<u>n-C₇H₁₆</u>	7.45
<u>n-C₈H₁₈</u>	7.55
<u>n-C₉H₂₀</u>	7.65
<u>n-C₁₀H₂₂</u>	8.0

It might be argued that the large solubility parameter of the solvents would lead to immiscibility in the case of the fluorocarbons, but since the molal volumes of these solvents are undoubtedly large the entropy effect due to volume disparity should be considered. The effect of differences in molal volumes is to decrease the positive deviations from Raoult's law and it is possible that the volume disparity is large enough to permit miscibility in spite of the large difference.

In the light of the volume disparity it would be

interesting to determine the effect of this factor upon the activity coefficient ratio of solutes in an extractive distillation solvent. Instead of using equation 3, the following equation as given by Hildebrand (12) will be used for the activity coefficients since a correction term for volume disparity is included.

$$\ln \gamma_1 = \frac{V_1}{RT} (\delta_1 - \delta_2)^2 \phi_2^2 + \ln \phi_1 / x_1 + \left(1 - \frac{V_1}{V_2}\right) \phi_2 \quad (74)$$

If we again make the assumption that the volume fraction of solvent is large enough that components 1 and 2 act independently of each other we can write for the activity coefficient ratio

$$\ln \gamma_1 / \gamma_2 = \frac{V_1}{RT} (\delta_1 - \delta_3)^2 \phi_3^2 - \frac{V_2}{RT} (\delta_2 - \delta_3)^2 \phi_3^2 + \left(\frac{V_2 - V_1}{V_3}\right) \phi_3 + \ln \frac{V_1}{V_2} \quad (75)$$

When the molal volumes of the solutes are approximately equal the last two terms in equation 75 are negligible and equation 75 reduces to equation 64. Thus while the volume correction does affect the individual activity coefficients, the relative volatility of the solutes is unaffected. The success of the Scatchard-Hildebrand Theory in predicting relative volatilities for extractive distillation is then due to the cancellation of errors in the individual activity coefficient expressions when the ratio of activity coefficients are

used. This fact was recognized by Reed (35) and was used by him to explain the success of the Scatchard-Hildebrand theory in predicting azeotropes (33) and relative volatilities in hydrocarbon systems.

CHAPTER X

EVALUATION OF METHODS OF SEPARATING FLUOROCARBON MIXTURES

This discussion will deal mainly with possible procedures for separation of fluorocarbon mixtures since separation procedures for hydrocarbon mixtures have been covered quite thoroughly by Rossini et al (37).

Distillation.--Several binary systems containing fluorocarbons have been investigated (5) (24) (49) with ideal solution behavior reported in all cases. Since fluorocarbon-fluorocarbon mixtures can be expected to follow ideal behavior, the relative volatility or the ease of separation depends upon the ratio of vapor pressures of the compounds to be separated.

Yen has shown that when fluorocarbon mixtures are distilled, laboratory distillation columns are approximately one-half as efficient as when hydrocarbon mixtures are distilled. A laboratory distillation column having 100 theoretical plates in a hydrocarbon separation would have approximately 50 theoretical plates in a fluorocarbon separation.

Azeotropic Distillation.--As would be expected from the large positive deviations exhibited by fluorocarbon-hydrocarbon mixtures, azeotropes are formed between fluoro-

carbons and hydrocarbons even when differences in normal boiling points are large. This azeotropic tendency has been exploited by Mair (23), who used fluorocarbons as azeotroping agents in separating paraffin and cycloparaffin hydrocarbons.

The C_7F_{16} and $C_8F_{16}O$ used in this work were each purified by azeotropic distillation with $n-C_7H_{16}$. Since the addition of a hydrocarbon azeotroping agent to a fluorocarbon mixture would also increase the efficiency of the distillation column, it is possible that azeotropic distillation holds some promise as a means of separating fluorocarbon mixtures.

Extractive Distillation.--It was shown earlier that some enhancement of the relative volatility of a fluorocarbon mixture could be obtained by employing a chlorofluorocarbon solvent for extractive distillation. Yen found chlorofluorocarbons to have column efficiencies slightly less than hydrocarbons, but approximately twice as large as fluorocarbons. In this case the added solvent would enhance the separation by increasing the relative volatility and by increasing the column efficiency.

The effect of the relative volatility and column efficiency upon the separation obtainable by distillation can be seen from an equation derived by Fenske (8).

$$\left(\frac{x_1}{x_2}\right)_D \bigg/ \left(\frac{x_1}{x_2}\right)_W = \alpha^N \quad (76)$$

Equation 76 applies for conditions of total reflux and constant α . The left hand side is a measure of the separation attainable in a column of N plates; a large value of the ratio on the left-hand side indicates good separation. The effect of increasing the column efficiency is to increase the number of theoretical plates (N); thus if both the relative volatility and the column efficiency are increased the resulting change in separation can be large.

Liquid Extraction.—We have seen earlier that separation of fluorocarbons by liquid extraction is not feasible where specific interactions between one component and the solvent are absent. Where a functional group is present in a fluorocarbon, there is the possibility that a solvent can be found which will be selective for this compound. An example of this type could be found in the system $C_8F_{16}O$ - $C_7F_{15}H$ - C_2H_5OH where $C_8F_{16}O$ and C_2H_5OH are practically immiscible while $C_7F_{15}H$ and C_2H_5OH are miscible even at temperatures as low as $-50^\circ C$. In this case there is undoubtedly a hydrogen bonding effect which would permit the separation of $C_7F_{15}H$ from $C_8F_{16}O$ by extraction with C_2H_5OH .

CHAPTER XI

CONCLUSIONS

The experimental work and discussion included in the previous sections of this dissertation provide the basis for the following conclusions.

1. The simple Scatchard-Hildebrand theory is inadequate for predicting excess free energies of mixing, heats of mixing, and volume changes in fluorocarbon-hydrocarbon mixtures.

2. The Scatchard-Hildebrand theory with the modifications introduced by Reed provides good estimates of the heat of mixing in fluorocarbon-hydrocarbon systems.

3. Good estimates of the excess free energy of mixing can be calculated from the Van Laar equation and binary solubility data.

4. Heats of mixing calculated from the Van Laar equation and solubility data are unreliable.

5. The excess free energy of mixing fluorocarbons with paraffin hydrocarbons can be estimated from an empirical correlation if values of the solubility parameters, ionization potentials, and molal volumes are available.

6. Comparison of the calculated and observed consolute temperature is not a good criterion for testing the applicability of the Scatchard-Hildebrand theory.

7. Mixtures of fluorocarbons with hydrocarbons exhibit large volume changes on mixing (in the order of 3 per cent of the total volume at 50 mole per cent). This volume change on mixing was found to increase with increasing temperature.

8. A negative excess entropy of mixing at constant volume can be used to explain the disagreement in some fluorocarbon-hydrocarbon systems between observed thermodynamic properties and those calculated from the Scatchard-Hildebrand theory.

9. The concept of clustering can be used to explain the negative values of the excess entropy of mixing at constant volume.

10. Scatchard-Hildebrand or Van Laar equations may be used to predict activities in ternary systems if the constants are determined empirically from the solubility data for two of the binary systems.

11. The Scatchard-Hildebrand equations can be used to predict relative volatilities in systems containing an extractive distillation solvent.

12. The possibility of separating a mixture of two fluorocarbons by liquid extraction is slight unless one fluorocarbon contains a functional group which will permit some sort of interaction with the solvent.

13. Future work should be directed toward the measurement and theoretical calculation of the excess entropy of mixing at constant volume.

14. The problem of theoretically calculating the volume change attending mixing remains unsolved. Some light may be shed upon this problem when a theory is developed which will predict the entropy term.

APPENDIX

I. Purity of Compounds Used

Hydrocarbons.--Most of the hydrocarbons used in this work were obtainable commercially in a reasonable degree of purity and were not further purified. The physical properties of these compounds are listed in Table VII along with the reported literature values.

Fluorocarbons.--Five fluorocarbon compounds were used in this work. The physical properties of which are listed in Table VIII. The physical properties of some of these fluorocarbons have been reported in the literature; these values are also included in Table VIII. Since the supply of some of the fluorocarbon compounds was limited it was necessary to recover some fluorocarbons from mixtures with hydrocarbons and repurify them. Where this was done the physical properties of both batches are recorded in Table VIII.

1. Perfluorocyclic oxide, $C_8F_{16}O$. This material was the major constituent in "Fluorochemical O-75" manufactured by the Minnesota Mining and Manufacturing Company. It is believed that this fluorocarbon is a five or six membered, oxygen-containing ring with side chains. This material was first fractionated in a laboratory distillation column having 60 theoretical plates

(when tested with hydrocarbons). The center cut from this fractionation was further purified by an azeotropic distillation with n-heptane. The fluorocarbon was then separated from the hydrocarbon by cooling the azeotrope to dry ice temperature where liquid phases were found having very low mutual solubility. The perfluorocyclic oxide was then freed from the small amount of remaining n-heptane by redistillation in a 30 theoretical plate column (when tested with hydrocarbons). A chromatograph of this purified material revealed only one peak.

2. Perfluoroheptane, C_7F_{16} . This material was a constituent of "Fluorochemical 101" marketed by the Minnesota Mining and Manufacturing Company and was purified by the same procedure as perfluorocyclic oxide. This purified material also exhibited only one peak when subjected to chromatographic analysis.

3. Perfluorotributyl amine, $(C_4F_9)_3N$. This material was the center cut obtained by fractionation of Minnesota Mining and Manufacturing Company's "Fluorochemical N-43" in a 60 theoretical plate column (when tested with hydrocarbons). Chromatographic analysis indicated that this material was a mixture of several components, probably isomers.

4. 1-Hydroperfluoroheptane, $C_7F_{15}H$. This material

was prepared in the Fluorine Research Laboratory by Dr. H. C. Brown by the decarboxylation of the sodium salt of perfluorooctanoic acid. This material was purified by simple distillation in a column having 60 theoretical plates (when tested with hydrocarbons).

5. Methyl perfluorooctanoate, $C_7F_{15}COOCH_3$. This material was also prepared by Dr. H. C. Brown from perfluorooctanoic acid and was purified by simple distillation in a 60 theoretical plate column (for hydrocarbons).

II. Thermocouple and Thermometer Calibration

All thermocouples used in this work were the copper-constantan type. Thermocouple readings were made with a Leeds and Northrup potentiometer No. 8662 which could be read to ± 0.001 millivolt.

1. Thermocouple in two liquid phase still. The calibration temperatures for this thermocouple were the ice point and the boiling points of methylcyclohexane at 757.45 and 381.05 mm pressure. The boiling points of methylcyclohexane at these pressures were determined from the Antoine equation given in reference 1. The potentiometer readings (in millivolts) at these temperatures were used to determine the constants in a three-constant equation. The calibration data and equation are given in Table IX.

2. Thermocouple in Solubility Cell. This thermocouple was calibrated against a thermocouple previously calibrated by Dr. T. M. Reed of the Fluorine Research Laboratory having the following calibration equation.

$$t = 0.050 + 24.91e - 0.3592e^2$$

The two thermocouples were immersed in a water bath and both readings were made at the same temperature. These millivolt readings are listed in Table IX along with the bath temperatures calculated from the above calibration equation. Since the two thermocouple readings were practically identical, the calibration equation for the thermocouple in the solubility cell was taken to be

$$t = 0.050 + 24.91e - 0.3592e^2$$

3. Thermometer in Temperature Bath. This mercury-in-glass thermometer was graduated in tenths of degree centigrade and could be read to $\pm 0.02^\circ$ C. This thermometer was calibrated against a thermocouple calibrated by the National Bureau of Standards. The calibration data are given in Table IX.

Pycnometer Calibration Data and Equations.--The calibration data for five pycnometers at several temperatures are tabulated in Table X. The pycnometers were designed by Lipkin (22) and were essentially U tubes with a

bulb in one arm. The arms were capillary tubes provided with etched graduations.

At a constant temperature each pycnometer was calibrated by determining the volumes corresponding to three different liquid heights in the capillary arms. The volume was related to the total liquid height by the following equation

$$V = V_0 + ah$$

The constants V_0 and a were determined by the method of least squares.

The volume of a pycnometer at a particular liquid height was determined from the weight of distilled mercury occupying the pycnometer and the density of mercury at that temperature. All weighings were corrected for air buoyancy. The pycnometers were kept in a constant temperature bath for approximately thirty minutes before the liquid heights were read. The constant temperature bath never varied more than 0.05° C. from the calibration temperature.

Vapor Pressure Measurements.---The vapor pressures of all of the pure fluorocarbons were determined over a range of temperatures by measuring the boiling temperature under various applied pressures. The still shown on Figure 9 and a boiling point still similar to that described by Quiggle, Tongberg, and Fenske (31) were used for these measurements. Calibrated thermocouples were used for temperature readings. The stills

were connected to a closed system containing a mercury manometer which could be read to 0.10 mm by means of a cathetometer. The experimental data are reported in Table XI and $\log p$ is plotted versus $1/T$ in Figure 1.

TABLE VII

PHYSICAL PROPERTIES OF HYDROCARBONS USED IN THIS WORK

Compound	Source	Refractive Index at 25° C.		Density gm/ml at 25° C.		Boiling Point ° C.	
		Experi- mental	Literature	Experi- mental	Literature	Experi- mental	Literature
n-Heptane	Dow	1.3852	(1) 1.38511	0.6798	(1) 0.67951	98.4	(1) 98.427
Methyl Cyclohexane	Matheson, Coleman, and Bell	1.4206	(1) 1.42058	0.76511	(1) 0.76506	100.9	(1) 100.934
Toluene	Baker and Adamson	--	(1) 1.49414	0.86232	(1) 0.86236	110.7	(1) 110.625
Carbon Tetra- chloride	Laboratory Supply	1.4567	(43) 1.4573	1.5844	(43) 1.5845	--	(43) 76.8
Ethanol	Laboratory Supply	1.3596	(1) 1.35941	0.79089	(1) 0.78506	78.2	(1) 78.33
2-Butanone	Matheson, Coleman, and Bell	1.3761	(1) 1.37643	0.7995	(1) 0.79970	79.6	(1) 79.59

TABLE VIII

PHYSICAL PROPERTIES OF FLUOROCARBONS USED IN THIS WORK

Compound	Refractive Index at 25° C.		Density gm/ml		Boiling Point ° C.	
	Experi- mental	Literature	Experi- mental	Literature	Experi- mental	Literature
Perfluoroheptane C_7F_{16}	1.2594	(28) 1.25818	1.7253	(28) 1.71802	82.1	82.5 ⁽²⁸⁾
Perfluorocyclic Oxide $C_8F_{16}O$	1.2602		1.7276			
	1.2770	--	1.7633	--	102.8	--
1-Hydroperfluoro- heptane $C_7F_{15}H$	1.2768		1.7634			
	1.2700	(25) 1.2713	1.7233	--	95.4	94-95 ⁽²⁵⁾
Perfluorotribu- tylamine (C_4F_9) ₃ N	1.2906	--	1.8772	--	177.6	--
Methylperfluoro- octanoate $C_7F_{15}COOCH_3$	1.3033	(41) 1.304	1.6967	(41) 1.684	160.8	158 ⁽⁴¹⁾

TABLE IX

THERMOCOUPLE AND THERMOMETER CALIBRATIONS

A. Thermocouple in Two Liquid Phase Still

Substance	Vapor Pressure mm	t ° C.	e Millivolts
Ice	--	0.00	0.000
Methylcyclohexane	757.45	100.82	4.311
Methylcyclohexane	381.05	78.16	3.274

Calibration equation: $t = 25.40e - 0.4672e^2$

B. Thermocouple in Solubility Cell

Solubility Cell Thermocouple Millivolts	Previously Calibrated Thermocouple Millivolts	Bath Temperature ° C.
1.724	1.728	42.0
2.340	2.340	56.4
2.344	2.344	68.0
3.273	3.266	77.6
3.353	3.353	79.5
3.140	3.146	74.9
3.016	3.016	71.9

Calibration operation: $t = 0.050 + 24.91e - 0.3592e^2$

TABLE IX
(Continued)

THERMOCOUPLE AND THERMOMETER CALIBRATIONS

C. Temperature Bath Thermometer

Thermometer Reading ° C.	Standard Thermocouple m.v.	Reading ° C.
0.04	0.0	0.0
20.00	1.023	19.90
24.96	1.289	25.00
30.57	1.580	30.56
37.73	1.964	37.86
47.23	2.471	47.44

TABLE X

PYCNOMETER CALIBRATIONS

Pycnometer No.	Calibration Temperature ° C.	Mass of Mercury gm.	Volume ml.	h, Sum of Liquid Height	Empirical Equations
100	25	136.6083	10.0937	12.71	$V = 9.9948 + 0.007782h$
		136.2601	10.0680	9.40	
		135.5923	10.0186	3.06	
101	25	136.4716	10.0836	13.31	$V = 9.9787 + 0.007883h$
		135.9787	10.0472	8.70	
		135.3102	9.9978	2.42	
51	25	65.9762	4.8748	13.10	$V = 4.7724 + 0.007823h$
		65.4239	4.8340	7.84	
		64.8817	4.7940	2.78	
1	40	68.7939	5.0969	10.15	$V = 5.0161 + 0.007960h$
		68.5161	5.0760	7.52	
		68.1134	5.0462	3.78	
1	45	68.7901	5.1012	10.72	$V = 5.0170 + 0.007861h$
		68.5123	5.0806	8.08	
		68.1097	5.0507	4.30	
1	50	68.7901	5.1058	11.28	$V = 5.0176 + 0.007818h$
		68.5123	5.0852	8.64	
		68.1097	5.0553	4.82	
1	55	68.8410	5.1142	12.32	$V = 5.0168 + 0.007919h$
		68.2914	5.0734	7.11	
		67.6230	5.0237	0.89	
1	60	68.8410	5.1188	12.90	$V = 5.0174 + 0.007877h$
		68.2914	5.0780	7.65	
		67.6230	5.0283	1.40	
2	40	69.7673	5.1690	12.26	$V = 5.0706 + 0.008010h$
		69.2219	5.1286	7.28	
		68.7600	5.0944	2.94	
2	45	69.7673	5.1737	12.78	$V = 5.0699 + 0.008113h$
		69.2219	5.1332	7.85	
		68.7600	5.0990	3.57	
2	50	69.7673	5.1783	13.32	$V = 5.0701 + 0.008111h$
		69.2219	5.1379	8.38	
		68.7600	5.1036	4.10	

TABLE XI

VAPOR PRESSURES OF PURE FLUOROCARBONS

Substance	Temperature ° C.	Pressure mm.	log P	$1/T (10^3)$ T in ° K.
Perfluoro- heptane C_7F_{16}	82.8	767.3	2.83497	2.8090
	82.4	759.0	2.88024	2.8121
	82.3	758.3	3.87984	2.8130
	81.8	745.8	2.87262	2.8169
	81.5	739.8	2.86911	2.8193
	79.7	698.7	2.84429	2.8337
	79.5	688.5	2.83790	2.8353
	77.6	650.1	2.81298	2.8506
	76.1	619.5	2.79204	2.8629
	75.9	616.4	2.78986	2.8645
	73.2	560.6	2.74865	2.8869
	71.2	522.4	2.71800	2.9036
	70.0	503.9	2.70234	2.9137
	65.0	419.5	2.62273	2.9569
	61.4	367.3	2.56502	2.9886
	56.8	310.0	2.49136	3.0303
	53.2	267.6	2.42749	3.0637
	49.2	226.5	2.35526	3.1017
	46.4	202.3	2.30814	3.1289

TABLE XI
(Continued)

VAPOR PRESSURES OF PURE FLUOROCARBONS

Substance	Temperature ° C.	Pressure mm.	log P	1/T (10 ³) T in ° K.
Perfluoro- cyclic Oxide C ₈ F ₁₆ O	42.5	171.1	2.23325	3.1676
	38.2	142.2	2.15290	3.2123
	33.5	115.5	2.06258	3.2605
	102.8	761.4	2.88161	2.6596
	97.3	639.1	2.80557	2.6991
	92.7	551.6	2.74162	2.7330
	86.5	448.7	2.65196	2.7878
	79.9	357.4	2.55315	2.8321
	74.0	288.8	2.46060	2.8802
	66.2	214.5	2.33143	2.9464
	60.4	169.5	2.22917	2.9976
	55.3	136.3	2.13450	3.0441
	52.5	121.1	2.08314	3.0703
	46.9	94.3	1.97451	3.1240
	39.3	66.5	1.82269	3.2000
	34.7	52.1	1.71642	3.2478
	30.5	42.4	1.62737	3.2927
Perfluorotri- butylamine (C ₄ F ₉) ₃ N	177.6	762.6	2.88230	2.2183
	173.4	675.6	2.82969	2.2391

TABLE XI
(Continued)

VAPOR PRESSURES OF PURE FLUOROCARBONS

Substance	Temperature ° C.	Pressure mm.	log P	1/T (10 ³) T in ° K.
	170.2	620.0	2.79239	2.2553
	165.4	539.1	2.73167	2.2800
	159.5	450.6	2.65379	2.3111
	154.8	390.3	2.59140	2.3364
	140.0	335.1	2.52517	2.3685
	139.4	229.9	2.36154	2.4237
Perfluorotri butylamine (C ₄ F ₉) ₃ N	131.1	172.4	2.23654	2.4734
	126.1	122.7	2.10072	2.5259
	115.2	94.0	1.97313	2.6123
	104.4	58.8	1.76960	2.6484
	95.0	40.6	1.60831	2.7160
	90.3	31.1	1.49248	2.7510
	85.3	23.5	1.37070	2.7893
	82.2	19.2	1.27217	2.8139
Methyl-perfluoro-octanoate C ₇ F ₁₅ COOCH ₃	158.5	716.3	2.85510	2.3164
	160.6	756.4	2.87877	2.3052
	159.8	739.4	2.86886	2.3095
	158.2	705.7	2.84862	2.3180
	155.4	650.7	2.81336	2.3332

TABLE XI
(Continued)

VAPOR PRESSURES OF PURE FLUOROCARBONS

Substance	Temperature	Pressure	log P	$\frac{1}{T} (10^3)$ T in ° K.
	152.6	601.0	2.77890	2.3485
	146.0	494.7	2.69430	2.3855
	138.2	387.2	2.58789	2.4307
	132.4	322.5	2.50856	2.4655
	124.8	249.3	2.39674	2.5126
	116.6	184.3	2.26548	2.5654
	110.8	146.9	2.16687	2.6042
	104.8	116.7	2.06700	2.6455
	99.2	94.4	1.97025	2.6853
	91.3	66.7	1.82380	2.7435
Methyl-per- fluoro- octanoate $C_7F_{15}COOCH_3$	86.0	52.8	1.72280	2.7840
	79.4	38.6	1.58629	2.8361
	72.3	27.3	1.43584	2.8944
	68.8	22.1	1.34361	2.9240
	65.0	18.3	1.26293	2.9557
1-hydroper- fluoro- heptane $C_7F_{15}H$	98.5	840.5	2.92454	2.6903
	97.2	807.0	2.90687	2.6997
	95.8	773.3	2.88835	2.7100
	95.1	753.4	2.87703	2.7151

TABLE XI
(Continued)

VAPOR PRESSURES OF PURE FLUOROCARBONS

Substance	Temperature ° C.	Pressure mm.	log P	1/T (10 ³) T in ° K.
	95.0	751.6	2.87599	2.7159
	94.9	750.8	2.87552	2.7173
	93.8	726.3	2.86112	2.7255
	90.6	655.3	2.81644	2.7495
	88.7	618.3	2.79120	2.7631
	85.2	543.9	2.73552	2.7901
	82.0	493.9	2.69364	2.8155

TABLE XII

SOLUBILITY DATA

Systems with Perfluoroheptane (C ₇ F ₁₆)			
Mole Fraction Carbon Tetrachloride	Unmixing Temperature ° C.	Mole Fraction n-heptane	Unmixing Temperature ° C.
0 .305	25.3	0 .153	16.5
.349	31.7	.236	31.3
.393	37.7	.324	40.5
.436	42.6	.387	44.8
.480	46.9	.485	48.2
.586	54.2	.582	49.4
.672	57.0	.684	49.5
.737	57.5	.803	47.1
.835	57.0	.865	42.1
.897	52.9	.904	34.2
.933	45.2	.924	28.3
.963	30.9	0 .948	17.6
0 .975	19.9		

TABLE XII
(Continued)

SOLUBILITY DATA

Systems with Perfluorocyclic Oxide ($C_8F_{16}O$)

x = Mole fraction of other component

t = Unmixing temperature °C.

Carbon Tetrachloride		n-Heptane		Methyl Cyclohexane		Toluene		2-Butanone		Ethanol	
x	t	x	t	x	t	x	t	x	t	x	t
.381	25.7	.123	5.8	.130	8.2	.093	25.6	.066	14.0	.004	31.3
.440	32.4	.229	26.1	.228	31.5	.140	59.1	.090	23.4	.017	42.6
.516	39.4	.289	33.2	.290	41.0	.278	77.5	.137	38.5	.021	46.0
.575	42.8	.359	39.8	.387	52.1	.361	89.3	.206	54.5	.028	58.6
.679	46.8	.440	43.8	.488	59.8	.491	103.1	.269	65.8	.039	61.1
.733	47.3	.480	45.6	.592	63.5	.594	109.4	.331	73.6	.052	65.0
.794	47.4	.547	45.8	.645	65.0	.696	114.0	.409	82.6	.117	81.4
.818	47.4	.642	46.9	.700	65.2	.802	113.2	.501	89.0	.201	98.6
.872	46.2	.686	46.7	.759	65.1	.899	105.2	.580	92.6	.268	109.4
.890	44.9	.694	46.0	.800	65.2	.945	94.0	.733	96.0	.372	121.2
.916	41.4	.763	45.3	.849	61.6	.968	76.2	.795	95.4	.975	109.0
.932	38.0	.835	42.0	.900	55.9	.978	62.8	.862	93.0	.993	65.5
.948	32.2	.906	31.0	.955	37.0	.990	39.0	.917	86.6	.998	12.5
.957	27.3	.950	14.8	.974	20.8	.749	114.0*	.959	71.0		

*Sealed tube determination.

TABLE XII
(Continued)

SOLUBILITY DATA

Systems with Perfluorocyclohexane Oxide ($C_8F_{16}O$)											
x = Mole fraction of other component t = Unmixing temperature ° C.											
Carbon Tetrachloride		n-Heptane		Methyl Cyclohexane		Toluene		2-Butanone		Ethanol	
x	t	x	t	x	t	x	t	x	t	x	t
								.978	55.1		
								.990	26.9		
								.992	14.8		

Systems with Perfluorobutylamine (C_4F_9) ₃ N			
n-heptane		toluene	
x	t	x	t
0.109	9.8	0.063	7.3
.215	40.5	.161	53.6
.312	58.3	.288	87.0
.409	69.2	.396	105.2
0.507	75.9	0.550	125.3

TABLE XII
(Continued)

SOLUBILITY DATA

Systems with Perfluorobutylamine (C_4F_9) ₃ N			
n-heptane		toluene	
x	t	x	t
0.607	80.0	0.767	140.4
.765	82.5	.888	140.6
.818	82.0	.951	132.0
.902	77.4	.981	110.1
.949	66.0	0.995	71.0
0.990	22.0		

Systems Containing Methyl Perfluoro-octanoate ($C_7F_{15}COOCH_3$)					
n-heptane		Methylcyclohexane		Toluene	
x	t	x	t	x	t
0.249	11.0	0.197	2.8	0.700	6.0
.347	20.5	.310	21.8		
.463	27.8	.428	33.8		
.545	30.2	.577	42.4		
0.626	32.8	0.666	44.8		

TABLE XII
(Continued)

SOLUBILITY DATA

Systems Containing Methyl Perfluoro-octanoate ($C_7F_{15}COOCH_3$)					
n-heptane		Methylcyclohexane		Toluene	
x	t	x	t	x	t
0.702	32.5	0.748	44.5		
.817	30.6	.824	43.5		
.896	23.3	.908	42.2		
0.949	12.5	.938	36.5		
		0.972	21.8		
Systems Containing 1-Hydroperfluoroheptane ($C_7F_{15}H$)					
n-heptane		Methylcyclohexane		Toluene	
x	t	x	t	x	t
0.210	12.3	0.193	17.8	0.408	12.8
.307	23.0	.323	37.0	.456	18.8
.405	28.6	.417	44.3	.511	24.5
.496	31.0	.504	48.0	.597	30.4
.628	32.5	.610	51.3	.672	34.0
.704	31.0	.705	52.5	.760	36.0
0.794	27.5	0.805	48.6	0.798	34.5

TABLE XII
(Continued)

SOLUBILITY DATA

Systems Containing 1-Hydroperfluoroheptane ($C_7F_{15}H$)					
n-heptane		Methylcyclohexane		Toluene	
x	t	x	t	x	t
0.903	14.0	0.888	41.3	0.844	32.0
		.940	26.8	.897	27.5
		0.971	6.0	0.951	11.0

TABLE XIII

COMPARISON OF CALCULATED AND OBSERVED CONSOLUTE
TEMPERATURES AND COMPOSITIONS

System	Consolute Temperature ($^{\circ}$ K.)			Composition		
	Observed	Equation 7	Equation 9	Observed	Equation 8	Equation 10
$\text{CH}_3\text{C}_6\text{H}_5\text{-C}_8\text{F}_{16}\text{O}$	386	377	324	0.73	0.77	0.78
$\text{CH}_3\text{C}_6\text{H}_5\text{-(C}_4\text{F}_9)_3\text{N}$	415	660	460	.82	.86	.87
$\text{CH}_3\text{C}_6\text{H}_5\text{-C}_7\text{F}_{15}\text{COOCH}_3$	279	256	220			
$\text{CH}_3\text{C}_6\text{H}_5\text{-C}_7\text{F}_{15}\text{H}$	309	266	236	.75	.74	.74
$\text{n-C}_7\text{H}_{16}\text{-C}_8\text{F}_{16}\text{O}$	320	130	123	.63	.67	.67
$\text{n-C}_7\text{H}_{16}\text{-C}_7\text{F}_{15}\text{COOCH}_3$	306	84	76	.67	.69	.69
$\text{n-C}_7\text{H}_{16}\text{-C}_7\text{F}_{15}\text{H}$	305	99	95	.61	.63	.63
$\text{n-C}_7\text{H}_{16}\text{-(C}_4\text{F}_9)_3\text{N}$	355	286	240	.79	.78	.79
$\text{CH}_3\text{C}_6\text{H}_{11}\text{-C}_8\text{F}_{16}\text{O}$	338	189	173	.74	.71	.71
$\text{CH}_3\text{C}_6\text{H}_{11}\text{-C}_7\text{F}_{15}\text{COOCH}_3$	318	124	111	.75	.73	.73
$\text{CH}_3\text{C}_6\text{H}_{11}\text{-C}_7\text{F}_{15}\text{H}$	325	140	132	.69	.68	.68
$\text{CH}_3\text{COC}_2\text{H}_5\text{-C}_8\text{F}_{16}\text{O}$	369	500	408	.75	.81	.82
$\text{CCl}_4\text{-C}_8\text{F}_{16}\text{O}$	321	292	242	.80	.78	.79
$\text{CCl}_4\text{-C}_7\text{F}_{16}$	331	310	252	.75	.78	.78
$\text{n-C}_7\text{H}_{16}\text{-C}_7\text{F}_{16}$	323	98	94	0.63	0.66	0.66

TABLE XIV

TOTAL VAPOR PRESSURE--TEMPERATURE DATA

t (° C.) Pressure mm.		t (° C.) Pressure mm.		t (° C.) Pressure mm.	
Sys- Perfluorocyclic tem: Oxide-Toluene		Perfluorocyclic Oxide-n-Heptane		Perfluorocyclic Oxide-Methyl- cyclohexane	
37.4	106.9	24.0	67.4	22.4	64.1
42.2	132.9	25.5	73.8	27.9	83.9
47.2	168.6	29.4	83.6	34.8	116.4
51.0	197.3	32.3	100.8	41.4	154.9
61.8	304.1	34.4	111.9	46.5	209.9
67.8	393.3	35.6	118.3	55.2	271.8
76.0	513.9	36.5	122.6	61.6	344.8
80.6	600.1	39.7	143.0	64.4	381.9
86.7	730.6	43.0	165.4	85.4	758.2
88.0	761.9	45.8	185.6		
		46.2	187.8		
		46.9	196.4		
Sys- Perfluorocyclic tem: Oxide-Carbon Tetrachloride		Perfluoroheptane- n-Heptane		Perfluoroheptane- Carbon Tetra- chloride	
27.3	147.5	26.2	117.6	27.8	194.8
28.6	157.1	28.8	130.9	30.0	216.1
30.0	167.8	31.5	151.0	32.7	242.9
31.3	180.2	33.9	169.1	36.8	287.0
33.0	191.7	34.0	166.8	40.6	336.2
37.2	227.8	36.4	187.0	43.3	373.9
41.5	268.9	36.6	189.0	46.9	427.2
43.5	290.9	38.7	207.4	49.7	469.4
45.0	308.4	41.1	228.9	52.3	517.7
46.2	324.0	44.7	264.2	54.6	562.1
46.2	321.7	46.6	286.1	57.1	613.4
		48.4	307.8	63.5	760.0
		49.5	320.5		

TABLE XV

COMPARISON OF VAN LAAR ACTIVITIES WITH ACTIVITY RANGE
CALCULATED FROM EQUATION 15a

t (° C.)	Equation 15a	Van Laar	t (° C.)	Equation 15a	Van Laar	t (° C.)	Equation 15a	Van Laar
Perfluorocyclic Oxide- n-Heptane			Perfluorocyclic Oxide- Toluene			Perfluorocyclic Oxide- Methycyclohexane		
25	0.782-0.880	0.849	40	0.925-0.934	0.892	30	0.850-0.898	0.834
30	0.775-0.903	0.827	50	0.916-0.928	0.865	35	0.828-0.886	0.818
35	0.769-0.926	0.810	60	0.869-0.885	0.850	40	0.814-0.879	0.786
40	0.763-0.959	0.782	70	0.836-0.857	0.822	50	0.771-0.865	0.754
45	0.761-1.0	0.762	80	0.819-0.847	0.784	60	0.760-0.916	0.701
Perfluorocyclic Oxide- Carbon Tetrachloride			Perfluoroheptane- n-Heptane			Perfluoroheptane- Carbon Tetrachloride		
30	0.666-0.724	0.705	25	0.824-0.862	0.855	30	0.756-0.808	0.760
35	0.652-0.843	0.675	30	0.828-0.875	0.844	35	0.765-0.826	0.736
40	0.619-0.861	0.643	35	0.827-0.887	0.828	40	0.761-0.834	0.709
45	0.569-0.903	0.606	40	0.810-0.883	0.805	45	0.729-0.819	0.684
			45	0.793-0.890	0.780	50	0.698-0.811	0.655

TABLE XVI

VOLUME OF MIXTURES OF PERFLUOROHEPTANE AND CARBON
TETRACHLORIDE; PERFLUOROCYCLIC OXIDE AND CARBON
TETRACHLORIDE; PERFLUOROCYCLIC OXIDE AND
n-HEPTANE; AND PERFLUOROHEPTANE
AND n-HEPTANE

Mole Fraction	Volume of Mixture (cc/mole)		
System: Perfluoroheptane-Carbon Tetrachloride			
Carbon Tetrachloride	50° C.	55° C.	60° C.
1.00	100.22	100.96	101.65
0.950	107.98	108.72	109.51
0.903		115.70	116.60
0.817			129.59
0.701			145.97
0.583		161.26	162.76
0.504	170.73	172.24	173.75
0.377	187.56	189.23	191.00
0.335	192.89	194.60	196.43
0.236	205.62	207.44	208.98
0.123	219.73	221.67	223.77
0	234.43	236.50	238.74
System: Perfluorocyclic Oxide-Carbon Tetrachloride			
Carbon Tetrachloride	40° C.	45° C.	50° C.
1.00	98.97	99.57	100.22
0.969	104.09	104.79	105.48
0.936	109.21	110.12	110.82

TABLE XVI
(Continued)

VOLUME OF MIXTURES OF PERFLUOROHEPTANE AND CARBON
TETRACHLORIDE; PERFLUOROCYCLIC OXIDE AND CARBON
TETRACHLORIDE; PERFLUOROCYCLIC OXIDE AND
n-HEPTANE; AND PERFLUOROHEPTANE
AND n-HEPTANE

Mole Fraction Carbon Tetrachloride	Volume of Mixture (cc/mole)		
	40° C.	45° C.	50° C.
0.905		114.90	115.72
0.845			125.11
0.768			136.62
0.701			146.80
0.631			157.30
0.553		167.30	168.66
0.469	177.96	179.36	181.13
0.397	188.19	189.66	191.18
0.329	197.54	199.09	200.70
0.253	208.07	209.68	211.37
0.161	220.36	222.07	223.85
0.087	230.15	231.92	233.77
0	241.30	243.18	245.08
System: Perfluorocyclic Oxide- <u>n</u> -Heptane			
<u>n</u> -Heptane	40° C.	45° C.	50° C.
1.00	150.15	151.14	152.14
0.972	153.40	154.43	155.48

TABLE XVI
(Continued)

VOLUME OF MIXTURES OF PERFLUOROHEPTANE AND CARBON
TETRACHLORIDE; PERFLUOROCYCLIC OXIDE AND CARBON
TETRACHLORIDE; PERFLUOROCYCLIC OXIDE AND
n-HEPTANE; AND PERFLUOROHEPTANE
AND n-HEPTANE

Mole Fraction <u>n</u> -Heptane	Volume of Mixture (cc/mole)		
	40° C.	45° C.	50° C.
0.943	156.79	157.84	158.94
0.925	158.89	160.00	161.14
0.898	162.06	163.22	164.40
0.867	165.23	166.50	167.74
0.825		170.88	172.20
0.801		175.72	177.11
0.706			184.33
0.596			195.16
0.502			204.09
0.418		210.10	211.91
0.349	214.34	216.12	217.96
0.287	219.53	221.32	233.16
0.213	225.93	227.31	229.61
0.146	230.95	232.77	234.68
0.073	236.23	238.09	240.00
0	241.27	243.12	245.04

TABLE XVI
(Continued)

VOLUME OF MIXTURES OF PERFLUOROHEPTANE AND CARBON
TETRACHLORIDE; PERFLUOROCYCLIC OXIDE AND CARBON
TETRACHLORIDE; PERFLUOROCYCLIC OXIDE AND
n-HEPTANE; AND PERFLUOROHEPTANE
AND n-HEPTANE

Mole Fraction	Volume of Mixture (cc/mole)		
System: Perfluoroheptane- <u>n</u> -Heptane			
<u>n</u> -Heptane	40° C.	45° C.	50° C.
1.0	150.29	151.27	152.30
0.942		157.72	158.83
0.900		162.73	163.92
0.803			172.67
0.799			173.24
0.715			180.61
0.614			189.58
0.579			192.68
0.500			198.93
0.393			208.19
0.299	211.37	213.25	215.20
0.227	216.48	218.36	220.31
0.147	221.69	223.63	225.62
0.092	225.90	227.84	229.88
0	230.29	232.28	234.30

TABLE XVII

TOTAL VOLUME CHANGE AND PARTIAL MOLAL VOLUME
CHANGE ON MIXING

x_1	ΔV^M cc/mole	x_1	$\Delta \bar{V}_1$ cc/mole	$\Delta \bar{V}_2$ cc/mole
System: $C_8F_{16}O-CCl_4$ at $50^\circ C$. Subscript 1 refers to CCl_4				
0.087	1.23	0.0	14.1	0.0
0.161	2.05	0.1	12.0	0.19
0.253	2.87	0.2	9.67	0.62
0.329	3.31	0.3	7.17	1.46
0.397	3.55	0.4	5.58	2.27
0.469	3.96	0.5	3.99	3.52
0.553	3.75	0.6	2.65	5.22
0.631	3.55	0.7	1.62	7.04
0.701	3.21	0.8	1.17	8.81
0.768	2.75	0.9	0.22	15.0
0.845	2.72	1.0	0.0	20.0
0.905	1.77			
0.936	1.27			
0.969	0.77			

TABLE XVII
(Continued)

TOTAL VOLUME CHANGE AND PARTIAL MOLAL VOLUME
CHANGE ON MIXING

x_1	ΔV^M cc/mole	x_1	$\Delta \bar{V}_1$ cc/mole	$\Delta \bar{V}_2$ cc/mole
System: C_7F_{16} - $\underline{n}$ - C_7H_{16} at 50° Subscript 1 refers to $\underline{n}$ - C_7H_{16}				
0.092	3.12	0.0	29.4	0
0.147	3.37	0.1	22.4	0.31
0.227	4.62	0.2	15.2	1.54
0.299	5.42	0.3	10.7	2.96
0.393	5.97	0.4	7.20	4.81
0.500	5.63	0.5	5.51	5.93
0.579	5.69	0.6	4.42	7.43
0.614	5.63	0.7	3.12	10.0
0.715	4.94	0.8	2.19	13.2
0.800	4.54	0.9	0.83	20.6
0.803	4.06	1.0	0	32.7
0.900	3.42			
0.942	1.77			

TABLE XVII
(Continued)

TOTAL VOLUME CHANGE AND PARTIAL MOLAL VOLUME
CHANGE ON MIXING

x_1	$\Delta \bar{V}^M$ cc/mole	x_1	$\Delta \bar{V}_1$ cc/mole	$\Delta \bar{V}_2$
System: $C_8F_{16}O$ - n - C_7H_{16} at 50° C. Subscript 1 refers to n - C_7H_{16}				
0.073	1.78	0.0	28.1	0.0
0.146	3.17	0.1	20.9	0.26
0.213	4.35	0.2	15.1	1.16
0.287	4.80	0.3	9.64	2.95
0.349	5.30	0.4	7.66	4.34
0.418	5.70	0.5	5.74	5.74
0.502	5.68	0.6	3.94	7.94
0.596	5.53	0.7	2.78	10.3
0.706	4.91	0.8	1.70	14.0
0.825	3.84	0.9	0.46	22.1
0.867	3.25	1.0	0.0	29.0
0.898	2.80			
0.925	2.00			
0.943	1.53			
0.972	0.77			

TABLE XVII
(Continued)

TOTAL VOLUME CHANGE AND PARTIAL MOLAL VOLUME
CHANGE ON MIXING

x_1	ΔV^M cc/mole	x_1	$\Delta \bar{V}_1$ cc/mole	$\Delta \bar{V}_2$
System: $C_7F_{16}-CCl_4$ at 60° C. Subscript 1 refers to CCl_4				
0.123	1.84	0.0	15.5	0.0
0.236	2.65	0.1	12.4	0.18
0.335	3.66	0.2	10.7	0.49
0.377	3.93	0.3	8.23	1.34
0.504	4.05	0.4	6.05	2.52
0.583	3.90	0.5	3.86	4.24
0.701	3.36	0.6	1.98	5.74
0.815	2.52	0.7	1.63	7.55
0.903	1.62	0.8	0.83	10.1
0.950	0.94	0.9	0.21	14.4
		1.0	0.0	18.3

TABLE XVIII

CALIBRATION DATA FOR ANALYSIS OF SYSTEMS: $C_7F_{16}-C_8F_{16}O-CCl_4$; $C_7F_{16}-C_8F_{16}O-n-C_7H_{16}$; AND $C_6H_5CH_3-C_6H_{11}CH_3-C_7F_{15}COOCH_3$

System: $C_7F_{16}-C_8F_{16}O-CCl_4$ Partitioning Liquid: Kel-F Acid Ester $Cl(CF_2CFCl)_3CF_2COOC_2H_5$ Helium Flow: 30 cc/min. Column Temperature: 80° C.			
Binary System $C_8F_{16}O-CCl_4$		Binary System $C_8F_{16}O-C_7F_{16}$	
Peak Height Fraction $C_8F_{16}O$	Weight Fraction $C_8F_{16}O$	Peak Height Fraction $C_8F_{16}O$	Weight Fraction $C_8F_{16}O$
0.329	0.840	0.634	0.760
0.774	0.775	0.846	0.910
0.450	0.438	0.404	0.527
0.718	0.702	0.242	0.333
0.922	0.918	0.124	0.179
0.170	0.161	0.637	0.760
0.115	0.119	0.403	0.527
0.078	0.077	0.236	0.333
0.046	0.044		
System: $C_7F_{16}-C_8F_{16}O-n-C_7H_{16}$ Partitioning Liquid: Kel-F Acid Ester $Cl(CF_2CFCl)_3CF_2COOC_2H_5$ Helium Flow: 30 cc/min. Column Temperature: 80° C.			
Binary System $C_8F_{16}O-C_7H_{16}$			
Peak Height Fraction $C_8F_{16}O$	Weight Fraction $C_8F_{16}O$		
0.861	0.933		
0.074	0.134		
0.029	0.060		
0.048	0.084		
0.778	0.883		
0.319	0.467		
0.154	0.243		

TABLE XVIII
(Continued)

CALIBRATION DATA FOR ANALYSIS OF SYSTEMS: $C_7F_{16}-C_8F_{16}O-CCl_4$; $C_7F_{16}-C_8F_{16}O-n-C_7H_{16}$; AND $C_6H_5CH_3-C_6H_{11}CH_3-C_7F_{15}COOCH_3$

System: $C_6H_5CH_3-C_6H_{11}CH_3-C_7F_{15}COOCH_3$
Partitioning Liquid: Silicone DC 550 and Stearic Acid on Celite
Nitrogen Flow: 30 cc/min.
Column Temperature: 95° C.

Binary System $C_6H_{11}CH_3-C_7F_{15}COOCH_3$		Binary System $C_6H_5CH_3-C_6H_{11}CH_3$	
Peak Height $C_7F_{15}COOCH_3$	Weight Fraction $C_7F_{15}COOCH_3$	Peak Height $C_6H_{11}CH_3$	Weight Fraction $C_6H_{11}CH_3$
0.752	0.886	0.660	0.630
0.404	0.466	0.537	0.528
0.152	0.132	0.926	0.938
0.326	0.361	0.781	0.790
0.440	0.522	0.635	0.618
0.323	0.361	0.727	0.703
0.578	0.712	0.935	0.939
0.262	0.224	0.493	0.344
0.575	0.712	0.795	0.807
0.766	0.886	0.492	0.344
0.423	0.466	0.655	0.630
0.135	0.132	0.590	0.528
0.676	0.783	0.929	0.938
0.286	0.279	0.363	0.282
0.545	0.636	0.470	0.396
0.350	0.361	0.424	0.334
0.257	0.224	0.710	0.703
0.678	0.783	0.792	0.807
		0.362	0.282

TABLE XIX

TIE LINE DATA

Top Phase			Bottom Phase		
w ₁	w ₂	w ₃	w ₁	w ₂	w ₃
System C ₇ F ₁₆ -C ₈ F ₁₆ O-C ₇ H ₁₆ at 30° C.					
0.245	--	0.755	0.930	--	0.070
--	0.297	0.703	--	0.925	0.075
0.179	0.142	0.679	0.530	0.395	0.075
0.200	0.119	0.681	0.593	0.333	0.074
0.236	0.080	0.683	0.700	0.227	0.073
0.262	0.046	0.692	0.784	0.140	0.076
0.043	0.280	0.677	0.146	0.775	0.079
0.096	0.220	0.684	0.304	0.619	0.077
0.176	0.142	0.682	0.528	0.400	0.072
System C ₇ F ₁₆ -C ₈ F ₁₆ O-CCl ₄ at 30° C.					
--	0.128	0.872	--	0.777	0.223
0.084	--	0.916	0.800	--	0.200
0.034	--	0.916	0.836	--	0.164
0.008	0.118	0.874	0.056	0.724	0.220
0.013	0.106	0.876	0.128	0.655	0.217
0.025	0.100	0.875	0.182	0.615	0.203
0.057	0.078	0.864	0.276	0.514	0.210
0.031	0.076	0.893	0.276	0.514	0.210
0.047	0.062	0.891	0.389	0.414	0.197
0.082	0.018	0.900	0.698	0.123	0.180
0.053	0.025	0.922	0.575	0.232	0.193
0.074	0.032	0.894	0.536	0.231	0.183
0.058	0.045	0.897	0.477	0.336	0.187
0.058	0.045	0.897	0.472	0.321	0.206
0.091	0.010	0.900	0.769	0.073	0.157
0.091	0.010	0.900	0.753	0.071	0.180
0.088	0.018	0.893	0.710	0.132	0.159
0.088	0.018	0.893	0.700	0.131	0.170
0.077	0.024	0.900	0.645	0.175	0.182
0.077	0.024	0.900	0.643	0.182	0.168

TABLE XIX
(Continued)

TIE LINE DATA

Top Phase			Bottom Phase		
w ₁	w ₂	w ₃	w ₁	w ₂	w ₃
System C ₆ H ₅ CH ₃ -C ₆ H ₁₁ CH ₃ -C ₇ F ₁₅ COOCH ₃ at 25° C.					
--	0.782	0.218	--	0.096	0.904
0.025	0.727	0.248	0.005	0.111	0.883
0.052	0.685	0.263	0.010	0.116	0.875
0.081	0.619	0.300	0.019	0.118	0.864
0.106	0.551	0.343	0.031	0.131	0.838
0.146	0.427	0.427	0.060	0.162	0.778
0.115	0.237	0.648	0.115	0.237	0.648
System C ₆ H ₅ CH ₃ -C ₆ H ₁₁ CH ₃ -C ₇ F ₁₅ COOCH ₃ at 10° C.					
--	0.950	0.050	--	0.055	0.945
0.286	0.534	0.180	0.053	0.077	0.870
0.371	0.346	0.283	0.128	0.092	0.780
0.401	0.235	0.364	0.196	0.094	0.710
0.415	0.233	0.352	0.192	0.091	0.717
0.242	0.606	0.152	0.024	0.076	0.900
0.131	0.755	0.112	0.017	0.077	0.906
0.242	0.596	0.162	0.040	0.082	0.878
0.402	0.218	0.374	0.266	0.101	0.673
0.308	0.114	0.578	0.308	0.114	0.578

TABLE XX

ACTIVITIES CALCULATED FROM EQUATION 59

δ 's Evaluated from Pure Compounds						δ 's Evaluated from Solubility Data					
a_1	a_1'	a_2	a_2'	a_3	a_3'	a_1	a_1'	a_2	a_2'	a_3	a_3'

System: $C_7F_{16}-C_8F_{16}O-CCl_4$ at $30^\circ C$.

0.68	0.96	0.23	0.54	0.08	0.16	0.97	0.96	0.58	0.57	0.19	0.16
0.70	0.95	0.16	0.38	0.15	0.31	0.97	0.96	0.41	0.40	0.36	0.32
0.74	0.95	0.05	0.12	0.26	0.54	0.97	0.99	0.13	0.13	0.62	0.57
0.72	0.95	0.07	0.17	0.24	0.50	0.97	0.96	0.17	0.18	0.53	0.53
0.73	0.96	0.10	0.25	0.20	0.42	0.97	0.98	0.24	0.27	0.48	0.44
0.71	0.96	0.14	0.35	0.16	0.33	0.97	0.97	0.35	0.37	0.39	0.35
0.71	0.96	0.17	0.42	0.11	0.26	0.97	0.98	0.43	0.45	0.28	0.27

System: $C_7F_{16}-C_8F_{16}O-n-C_7H_{16}$ at $30^\circ C$.

0.34	0.90	0.10	0.46	0.07	0.31	0.94	0.95	0.55	0.50	0.39	0.33
0.33	0.90	0.12	0.51	0.06	0.26	0.94	0.94	0.61	0.55	0.33	0.28
0.33	0.90	0.14	0.60	0.04	0.18	0.94	0.95	0.72	0.64	0.22	0.19
0.34	0.90	0.15	0.67	0.02	0.11	0.94	0.96	0.81	0.71	0.12	0.12
0.35	0.90	0.03	0.13	0.15	0.62	0.94	0.97	0.14	0.14	0.79	0.68
0.35	0.90	0.06	0.27	0.11	0.49	0.94	0.96	0.31	0.29	0.63	0.53
0.33	0.90	0.10	0.46	0.07	0.32	0.94	0.95	0.55	0.50	0.39	0.34

Note: Subscript 2 refers to C_7F_{16}
 Subscript 3 refers to $C_8F_{16}O$

TABLE XXI

ACTIVITIES CALCULATED FROM EQUATION 61

a_1	a_1'	a_2	a_2'	a_3	a_3'
System: $C_7F_{16}-C_8F_{16}O-CCl_4$ at $30^\circ C$.					
0.63	0.57	0.97	0.98	0.17	0.17
0.44	0.41	0.97	0.98	0.33	0.32
0.14	0.13	0.97	0.99	0.56	0.57
0.19	0.18	0.96	0.98	0.52	0.52
0.26	0.27	0.97	0.99	0.43	0.44
0.37	0.37	0.97	0.99	0.35	0.35
0.48	0.45	0.97	1.00	0.26	0.27
System: $C_7F_{16}-C_8F_{16}O-n-C_7H_{16}$ at $30^\circ C$.					
0.54	0.49	0.94	0.95	0.37	0.34
0.61	0.55	0.94	0.96	0.32	0.29
0.72	0.64	0.94	0.95	0.21	0.19
0.79	0.72	0.94	0.95	0.12	0.12
0.13	0.14	0.94	0.95	0.74	0.69
0.30	0.29	0.94	0.95	0.58	0.54
0.54	0.49	0.94	0.95	0.37	0.35

Note: Subscript 1 refers to C_7F_{16}
 Subscript 3 refers to $C_8F_{16}O$

TABLE XXII

CHARACTERISTICS OF CHROMATOGRAPHY COLUMNS
USED IN EXTRACTIVE DISTILLATION STUDIES

Column Number	Stationary Solvent Phase	Vapor Pressure of Solvent	Milliliters of Solvent Per Gram of Celite	Grams of Packing Per Meter	Interstitial Column Volume, cc
505-112	Kel-F Oil 1	17 mm at 100° C.	0.50	14.1	9
505-136	Kel-F Oil 3	1 mm at 100° C.	0.50	17.0	8
505-137	Kel-F Oil 10	0.1 mm at 100° C.	0.70	16.3	5
505-135	Perfluoro-kerosene	Boiling Point 170-230° C.	0.25	20.7	22

TABLE XXIII

APPEARANCE TIME OF C_7F_{16} , $C_8F_{16}O$, $n-C_7H_{16}$ AND $C_6H_{11}CH_3$ IN THE
VARIOUS PARTITIONING LIQUIDS

Partitioning Liquid	t ° C.	Carrier Gas Flow Rate cc/min.	Appearance Time (min.)			
			C_7F_{16}	$C_8F_{16}O$	$n-C_7H_{16}$	$C_6H_{11}CH_3$
Kel-F Oil 1	35	60	11.5	29.9	37.8	42.5
Kel-F Oil 3	35	60	12.3	32.3	--	--
Kel-F Oil 3	80	25	7.08	14.8	22.7	27.6
Kel-F Oil 10	35	57	6.75	18.3	26.5	29.5
Kel-F Oil 10	80	25	5.08	10.9	16.8	20.2
Perfluoro-kerosene	35	30	18.7	48.2	--	--

TABLE XXIV

RELATIVE VOLATILITY OF THE $C_7F_{16}-C_8F_{16}O$ -SOLVENT AND $n-C_7H_{16}-C_6H_{11}CH_3$ -SOLVENT SYSTEMS

Solvent	t ° C.	Relative Volatility	
		$C_7F_{16}-C_8F_{16}O$	$n-C_7H_{16}-C_6H_{11}CH_3$
No solvent	35	2.34	1.003
	80	1.96	1.057
Kel F Oil 1	35	2.60	1.12
Kel F Oil 3	35	2.62	--
	80	2.12	1.22
Kel F Oil 10	35	2.70	1.11
	80	2.20	1.21
Perfluoro-kerosene	35	2.58	--

TABLE XXV

ACTIVITY COEFFICIENT RATIOS BASED ON AVERAGE RELATIVE VOLATILITY FOR ALL SOLVENTS

System	t ° C.	p_1^0/p_2^0	γ_1/γ_2
$C_7F_{16}-C_8F_{16}O$ -Solvent	35	2.34	1.11
	80	1.96	1.10
$n-C_7H_{16}-CH_3C_6H_{11}$ -Solvent	35	1.003	1.11
	80	1.057	1.14

TABLE XXVI

PROPERTIES OF PURE COMPOUNDS FOR USE IN EQUATION 64

Compound	t, ° C.	σ (cal./cc) ^{1/2}	V (cc/mole)
C ₇ F ₁₆	35	5.93 ^a	228 ^c
	80	5.41 ^a	248 ^d
C ₈ F ₁₆ O	35	6.05 ^a	240 ^c
	80	5.52 ^a	259 ^e
n-C ₇ H ₁₆	35	7.31 ^b	149 ^f
	80	6.70 ^b	159 ^f
C ₆ H ₁₁ CH ₃	35	7.70 ^b	130 ^f
	80	7.20 ^b	137 ^f

^aDetermined from vapor pressure and density data of this work.

^bT. M. Reed private communication.

^cThis work.

^dExtrapolated from density temperature data of this work.

^eMinnesota Mining and Manufacturing Company data.

^fReference 1.

TABLE XXVII

DATA FOR USE IN EQUATIONS 37, 40, AND 46

Partial molal volumes: Table XVII
 Coefficient of Thermal Expansion, α : Figures 32-35
 Excess free energy of mixing, ΔF^E : Figures 17-19 and from
 Van Laar equation using constants from Figure 9
 Volume change on mixing, ΔV^M : Figures 23-26

Compound	Temperature, ° K.	Solubility Parameter σ	Molal Volume cc/mole	ΔE^V Energy of Vaporization cal./mole	Ionization Potential Volts	a for Use in Equation 47, 12 = atm 12
C ₇ F ₁₆	303	5.927 ^a	224 ^b	8051 ^d	17.6 ^e	101.1 ^h
C ₇ F ₁₆	323	5.694 ^a	234 ^b	7631 ^d	17.6 ^e	101.1 ^h
C ₇ F ₁₆	333	5.554 ^a	238 ^b	7375 ^d	17.6 ^e	101.1 ^h
n-C ₇ H ₁₆	323	7.107 ^a	152 ^c	7795 ^d	10.35 ^f	54.6 ⁱ
i-C ₈ H ₁₈	303	6.855 ^a	166 ^c	7800 ^d	10.29 ^e	83.8 ^j
CCl ₄	333	8.112 ^a	102 ^b	6689 ^d	11.0 ^g	31.5 ^h

^aT. M. Reed private communication.

^bThis work.

^cReference 1.

^dCalculated from solubility parameter and molal volume.

^eEstimated by method of Reference 34.

^fReference 21.

^gReference 45.

^hReference 20.

ⁱReference 46.

^jCalculated from Volume-Temperature data Reference 1 and Volume-Pressure data Reference 3.

TABLE XXVIII

DATA USED IN ESTABLISHING EMPIRICAL CORRELATION
FOR EXCESS FREE ENERGY

System	Type of Data	Temperature ° K.	K in Equations 50 and 51	$[\]^*$	$Z(10^3)$	Reference
$C_7F_{16}-i-C_8H_{18}$	Free Energy	303	7.00	3.95	2.54	26
$C_7F_{16}-3-CH_3C_7H_{15}$	Solubility	343	7.67	5.31	1.28	27
$C_7F_{16}-n-C_8H_{18}$	Solubility	341	6.50	5.86	0.32	9
$C_7F_{16}-n-C_7H_{16}$	Solubility	328	7.02	5.63	0.76	This work
$C_7F_{16}-n-C_6H_{14}$	Solubility	302	8.18	4.94	2.18	10
$C_7F_{16}-3-CH_3C_5H_{11}$	Solubility	292	8.12	4.32	3.01	10
$C_7F_{16}-2,2(CH_3)_2C_4H_8$	Solubility	273	6.20	4.34	1.57	10
$C_7F_{16}-2,3(CH_3)_2C_4H_8$	Solubility	283	6.35	4.87	1.06	10
$C_5F_{12}-n-C_6H_{14}$	Solubility	288	7.45	5.82	0.97	7
$C_5F_{12}-2-CH_3C_5H_{11}$	Solubility	273	7.24	4.15	2.71	7
$C_5F_{12}-3-CH_3C_5H_{11}$	Solubility	278	7.34	3.63	3.67	7
$C_5F_{12}-2,2(CH_3)_2C_4H_8$	Solubility	257	6.92	3.35	4.12	7
$C_5F_{12}-2,3(CH_3)_2C_4H_8$	Solubility	269	7.18	3.94	3.05	7
$C_5F_{12}-n-C_5H_{12}$	Free Energy	266	7.51	4.43	2.63	39
$C_4F_{10}-n-C_4H_{10}$	Free Energy	246	7.72	5.44	1.70	40

$$* [\] = [(\delta_1 - \delta_2)^2 + 2\delta_1\delta_2(1 - f_D^f)]$$

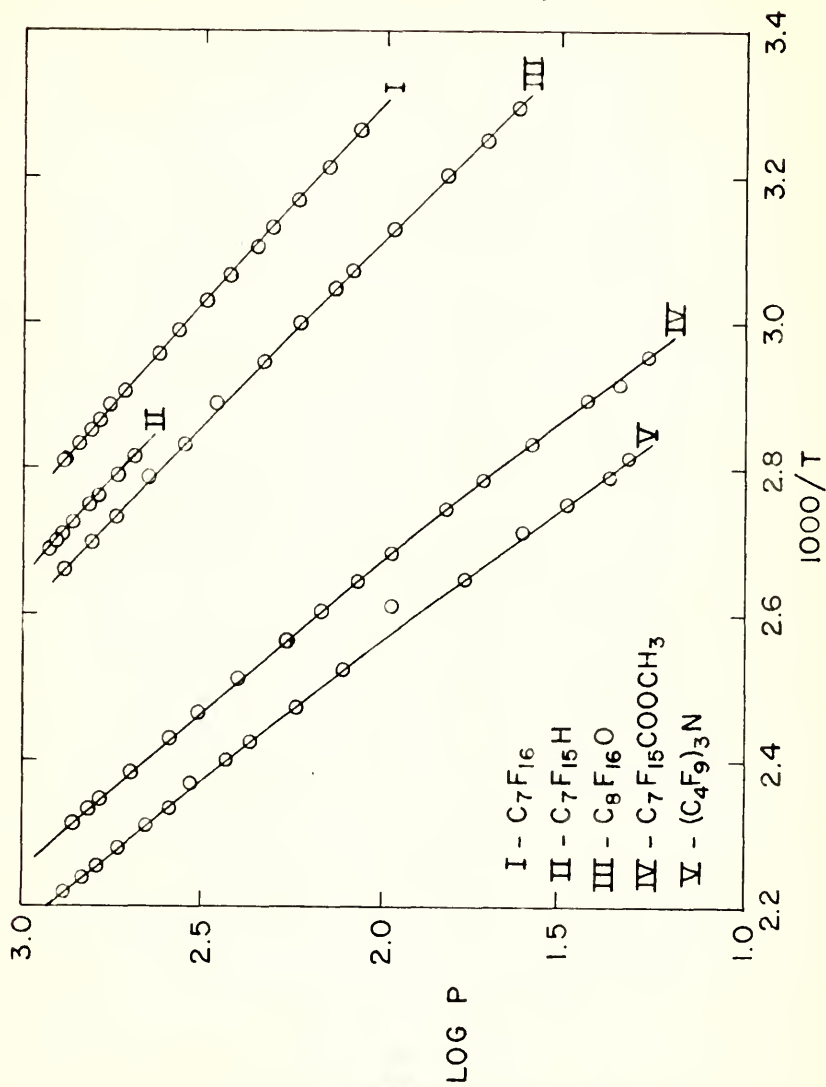


FIGURE 1. VAPOR PRESSURE DATA FOR FLUOROCARBONS

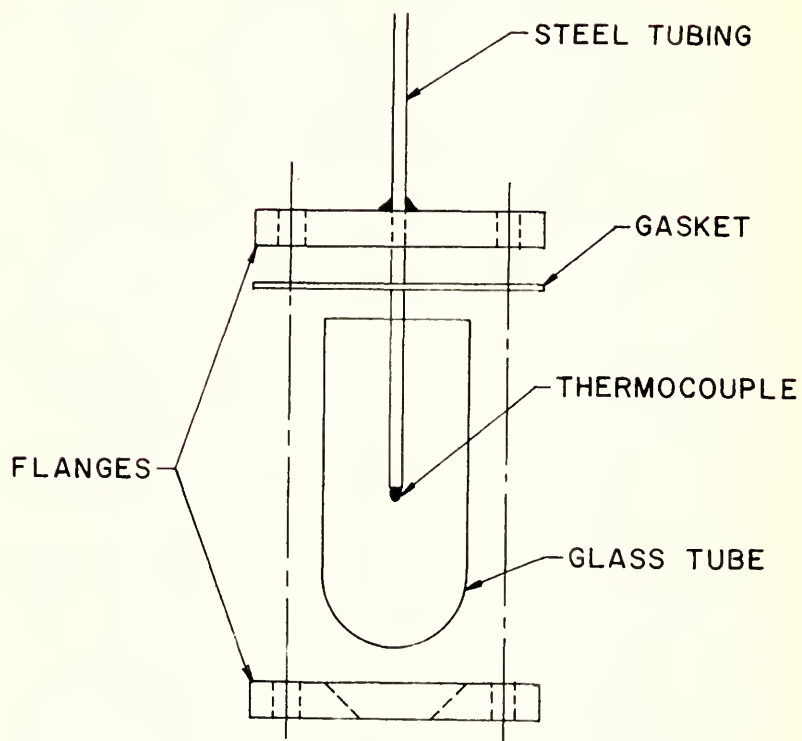
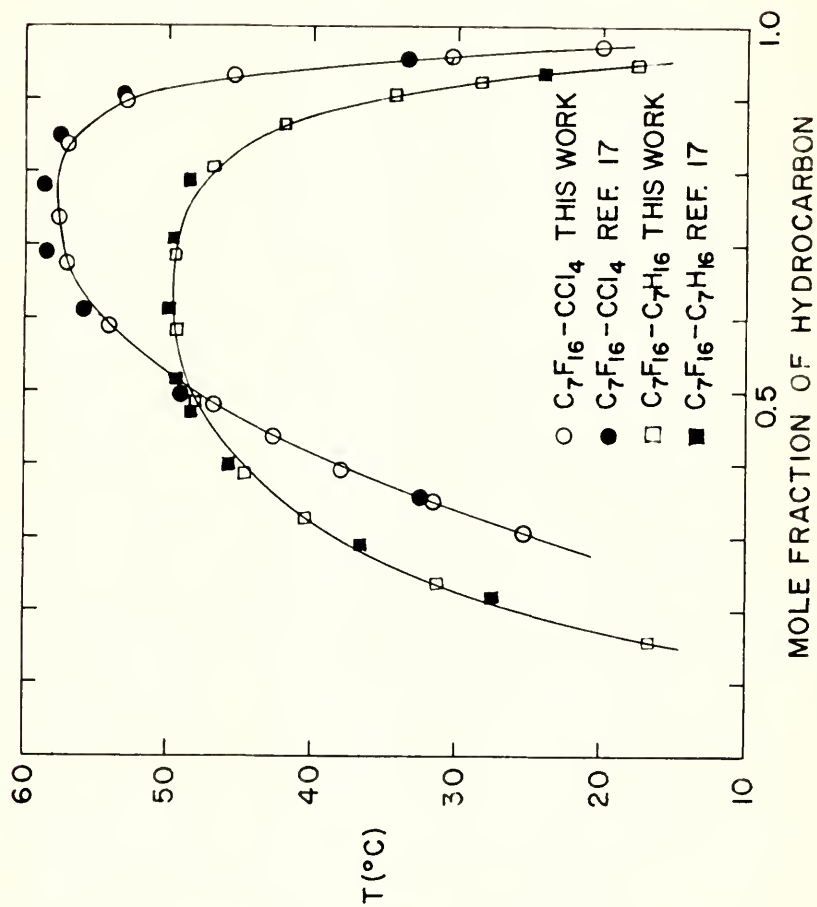


FIGURE 2.
SOLUBILITY CELL



MOLE FRACTION OF HYDROCARBON

FIGURE 3. BINARY SOLUBILITY CURVES
SYSTEMS CONTAINING C_7F_{16}

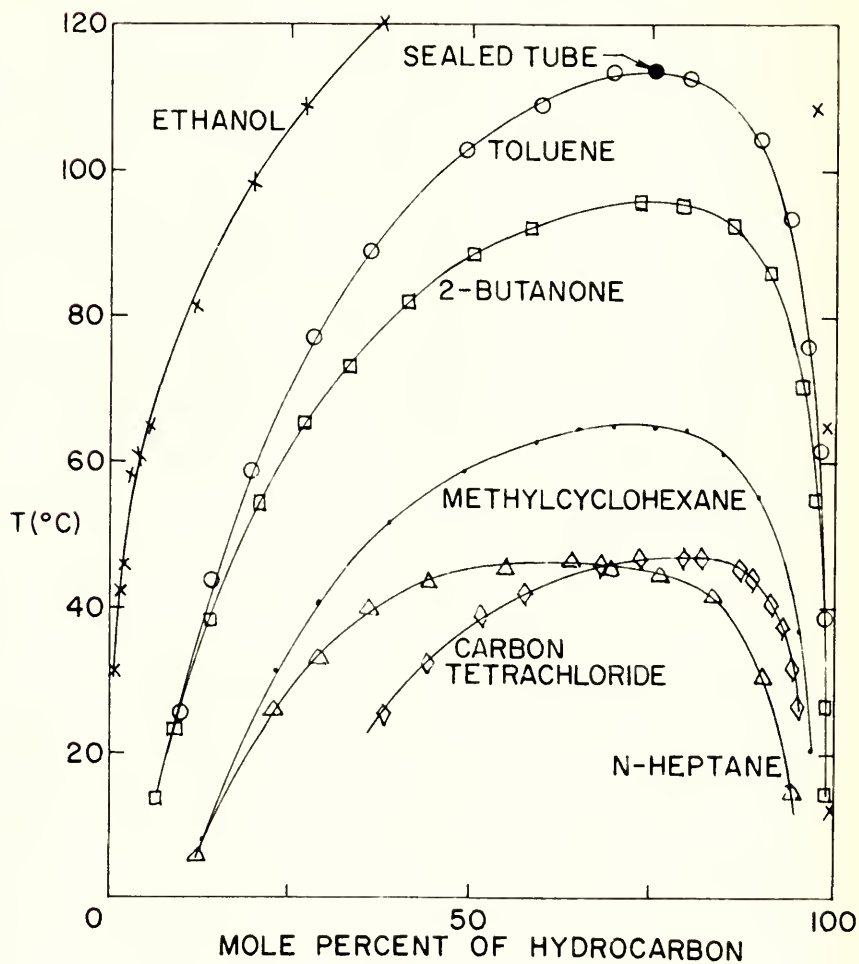


FIGURE 4. BINARY SOLUBILITY CURVES
SYSTEMS CONTAINING $C_8F_{16}O$

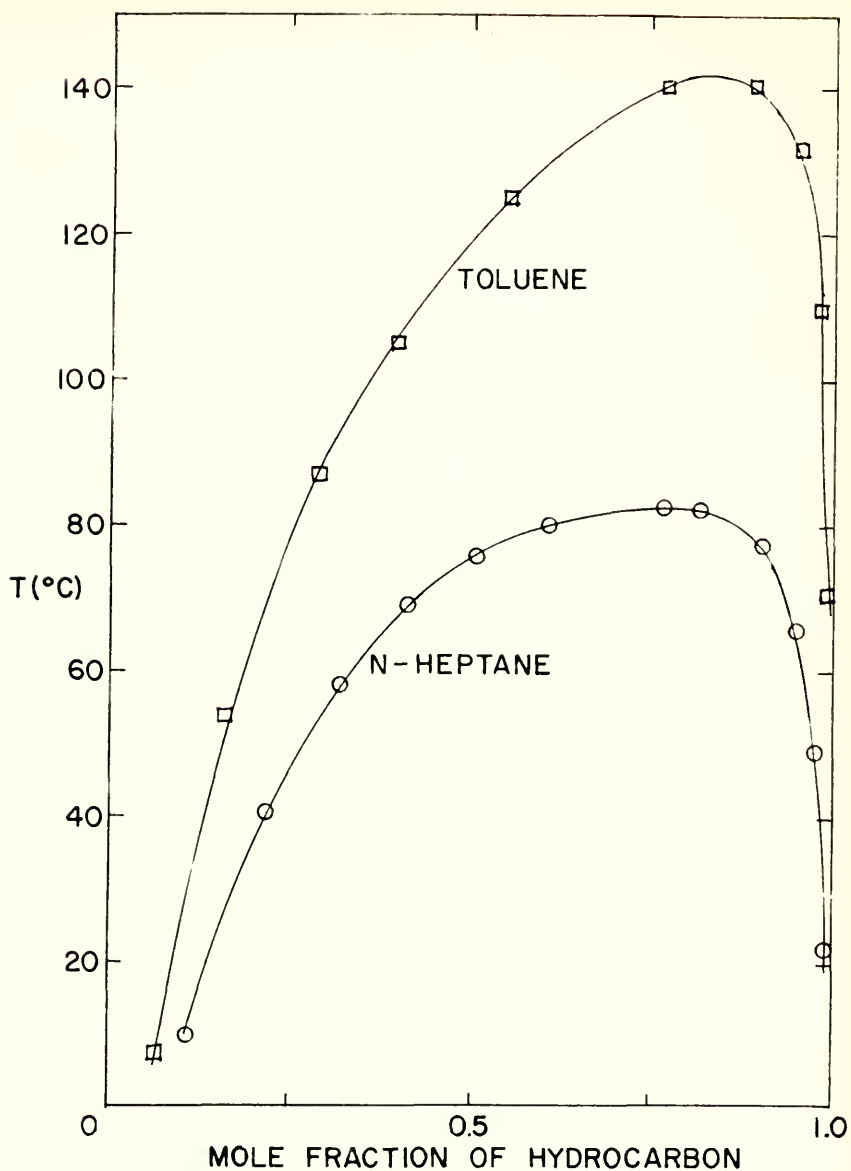


FIGURE 5. BINARY SOLUBILITY CURVES
SYSTEMS CONTAINING $(C_4F_9)_3N$

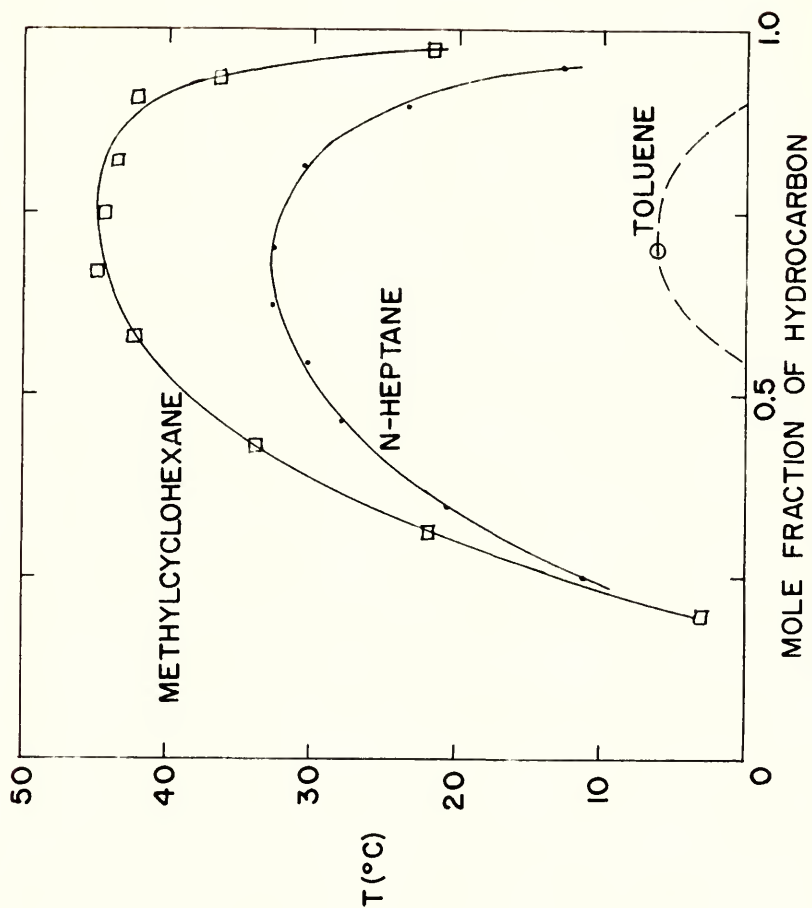


FIGURE 6. BINARY SOLUBILITY CURVES
SYSTEMS CONTAINING $C_7F_{15}COOCH_3$

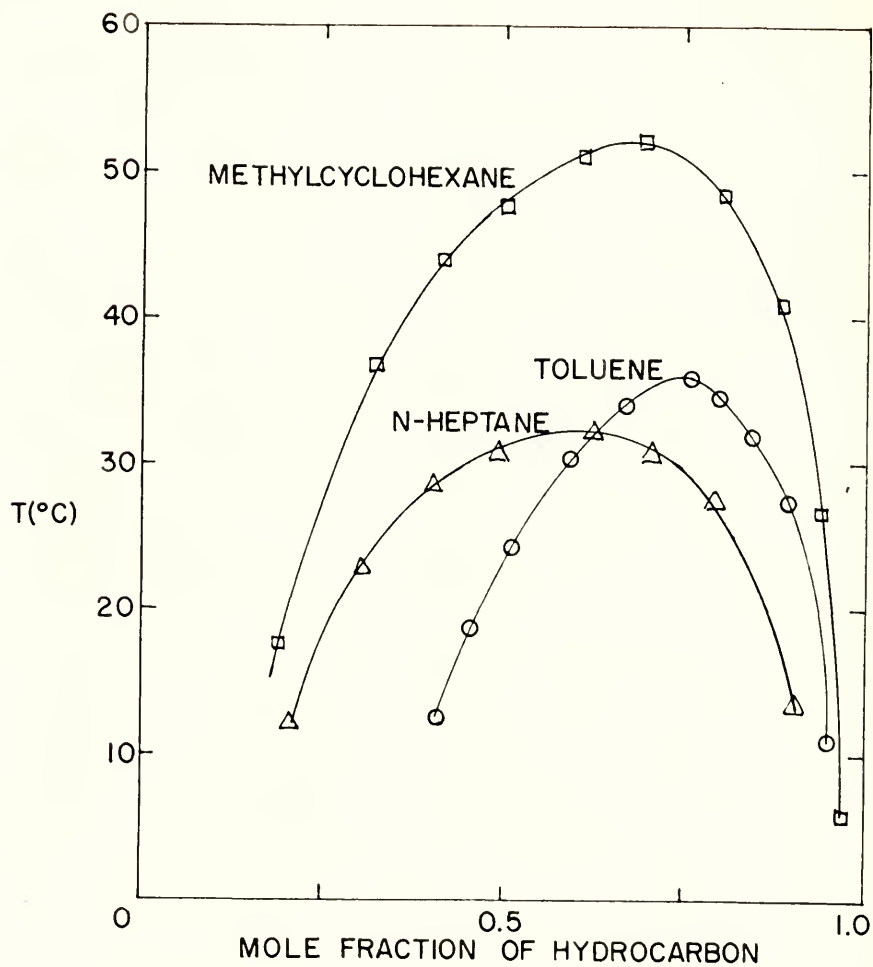


FIGURE 7. BINARY SOLUBILITY CURVES
SYSTEMS CONTAINING $C_7F_{15}H$

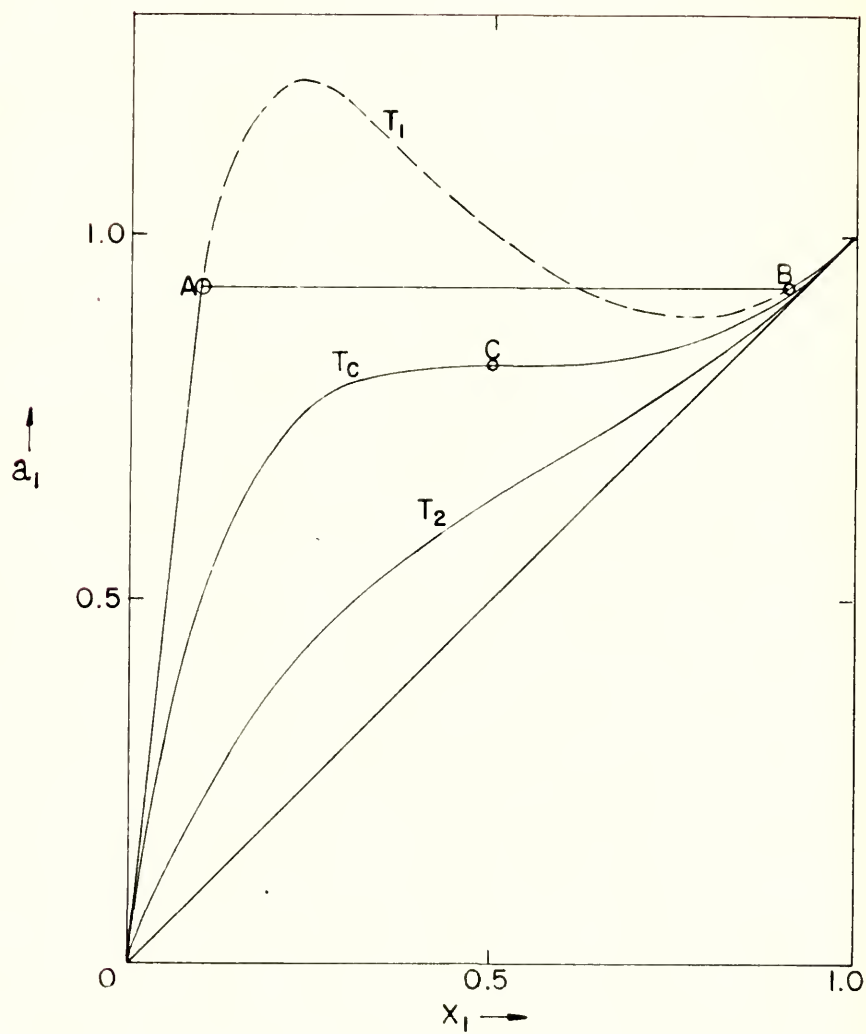


FIGURE 8. ACTIVITY ISOTHERMS

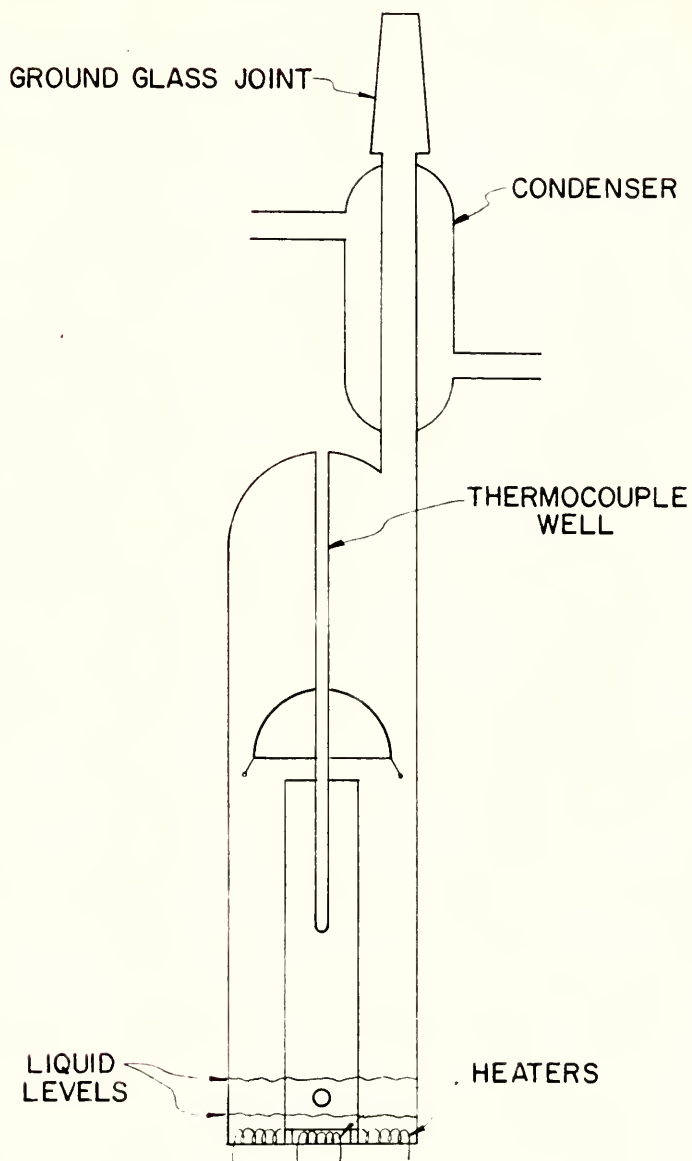


FIGURE 9. TWO LIQUID PHASE STILL

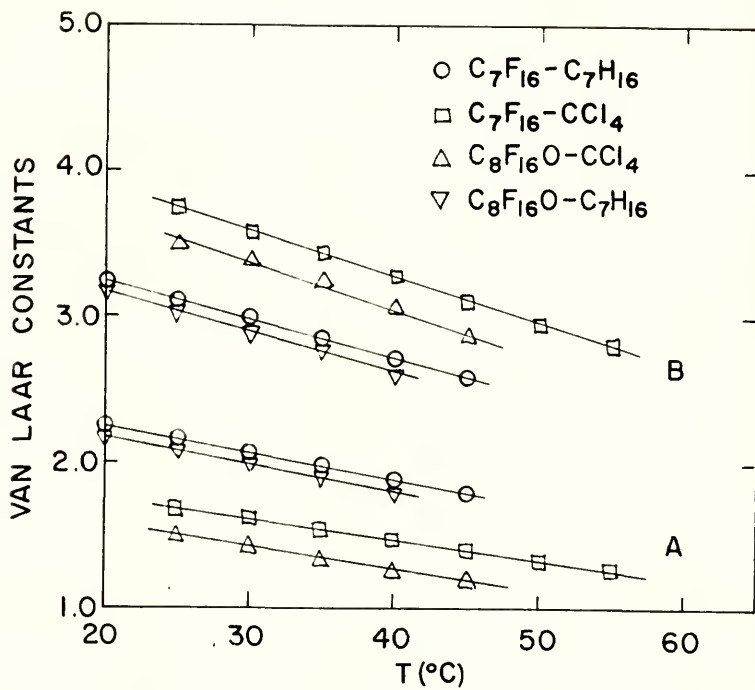


FIGURE 10. VAN LAAR CONSTANTS
VERSUS TEMPERATURE

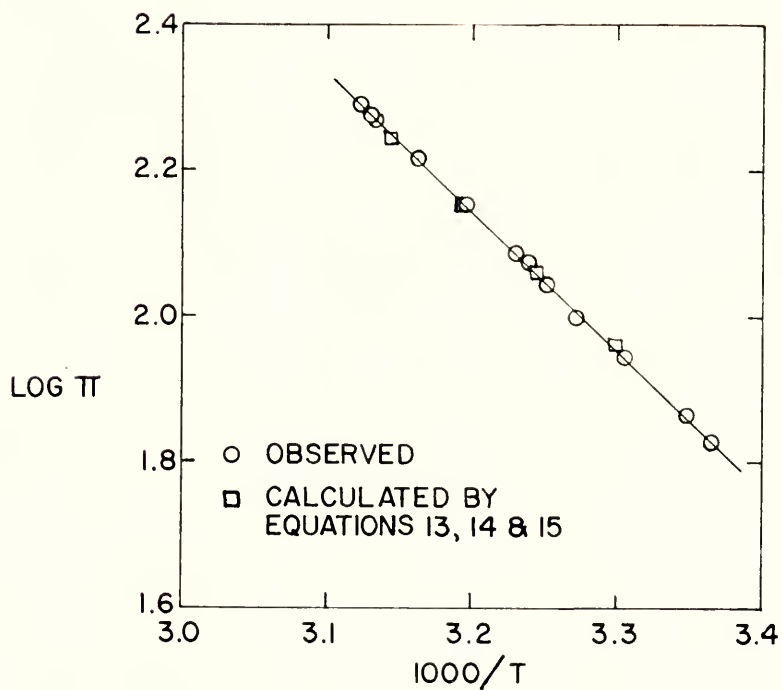


FIGURE 11. TOTAL VAPOR PRESSURE PLOT
SYSTEM: PERFLUOROCYCLIC OXIDE-
N-HEPTANE

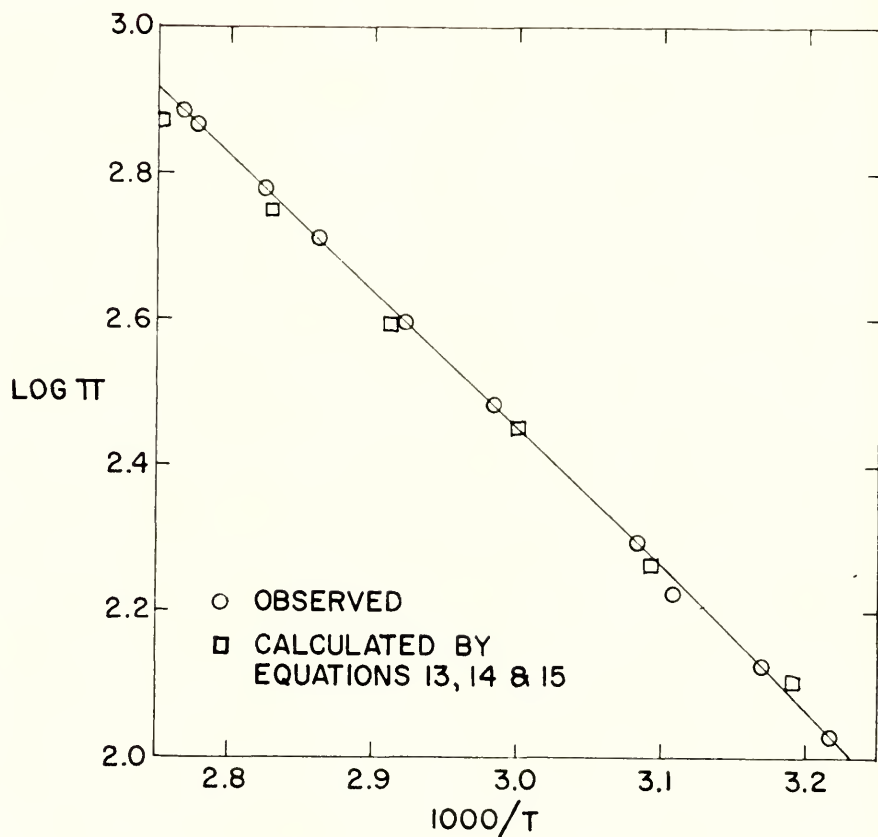


FIGURE 12. TOTAL VAPOR PRESSURE PLOT
SYSTEM: PERFLUOROCYCLIC OXIDE-
TOLUENE

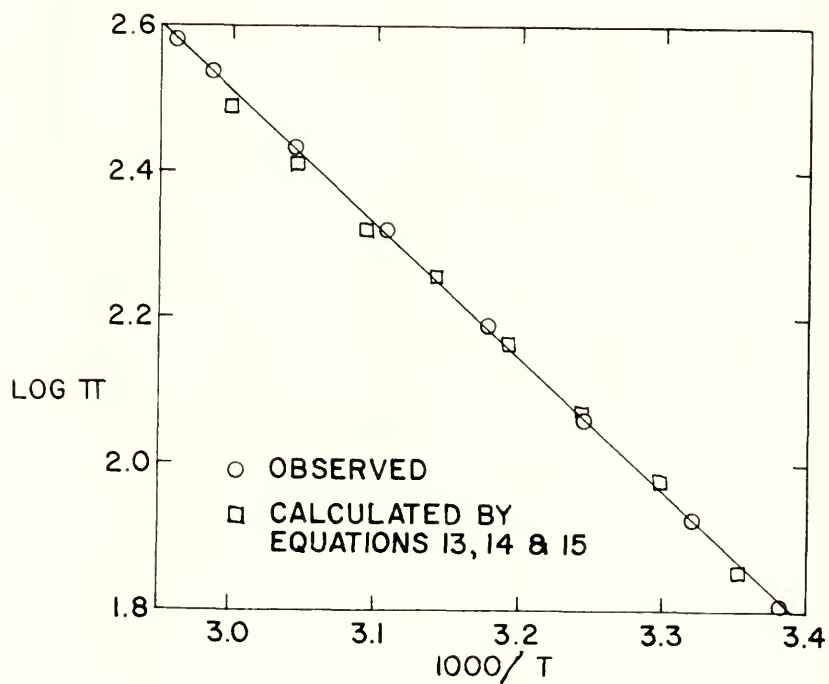


FIGURE 13. TOTAL VAPOR PRESSURE PLOT
SYSTEM: PERFLUOROCYCLIC OXIDE-
METHYLCYCLOHEXANE

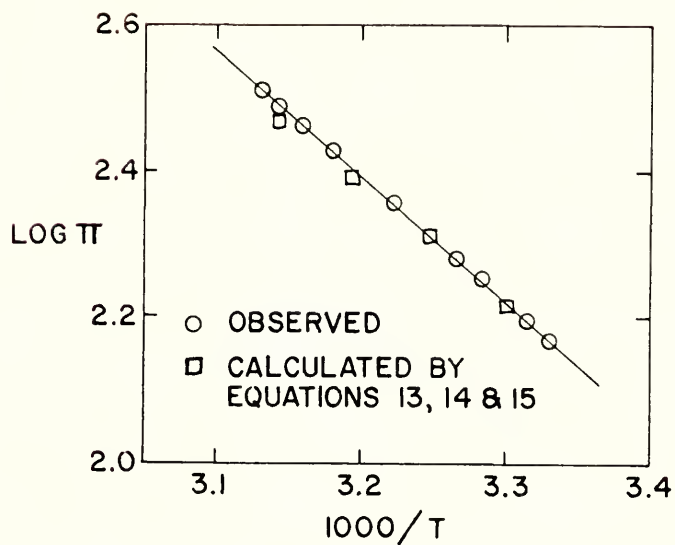


FIGURE 14. TOTAL VAPOR PRESSURE PLOT
SYSTEM: PERFLUOROCYCLIC OXIDE -
CARBON TETRACHLORIDE

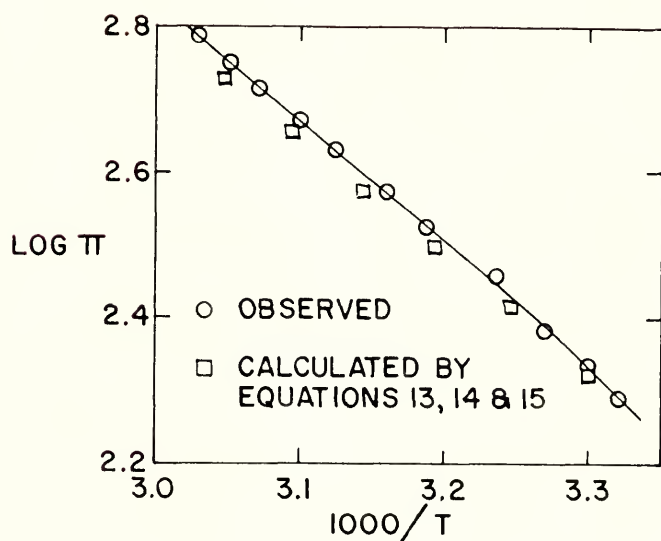


FIGURE 15. TOTAL VAPOR PRESSURE PLOT
SYSTEM: PERFLUOROHEPTANE-
CARBON TETRACHLORIDE

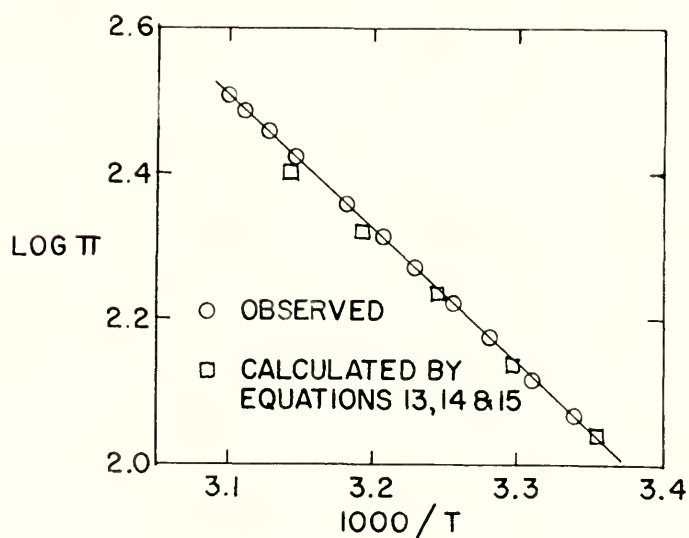


FIGURE 16. TOTAL VAPOR PRESSURE PLOT
SYSTEM: PERFLUOROHEPTANE -
N-HEPTANE

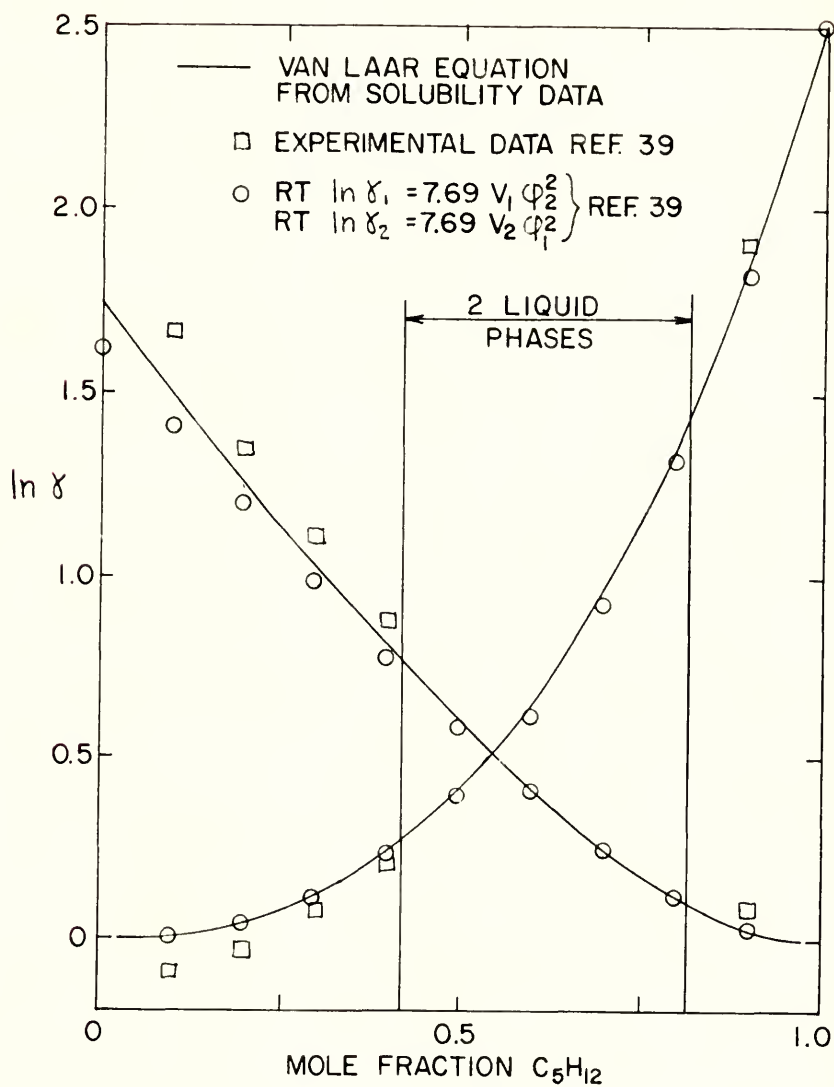


FIGURE 17. ACTIVITY COEFFICIENTS
 SYSTEM: C_5H_{12} - C_5F_{12}
 $T = 262.4^\circ K$

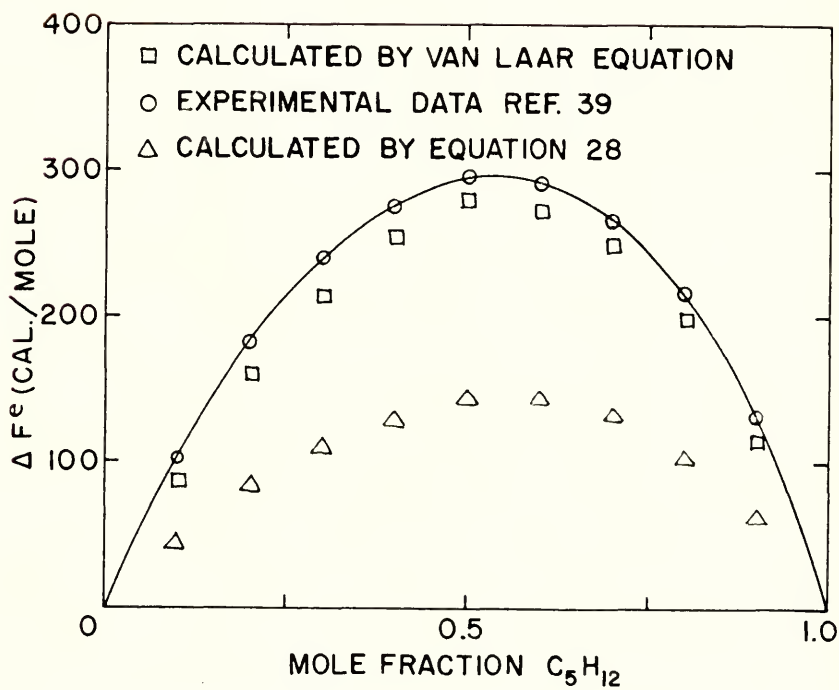


FIGURE 18. EXCESS FREE ENERGY OF MIXING
SYSTEM: $C_5F_{12}-C_5H_{12}$

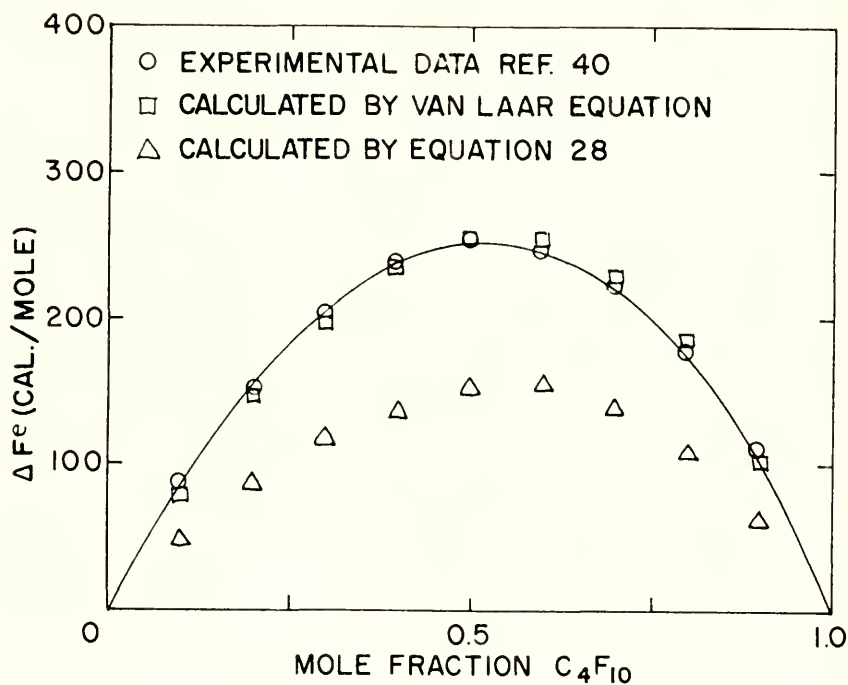


FIGURE 19. EXCESS FREE ENERGY OF MIXING
SYSTEM: C_4F_{10} - C_4H_{10}

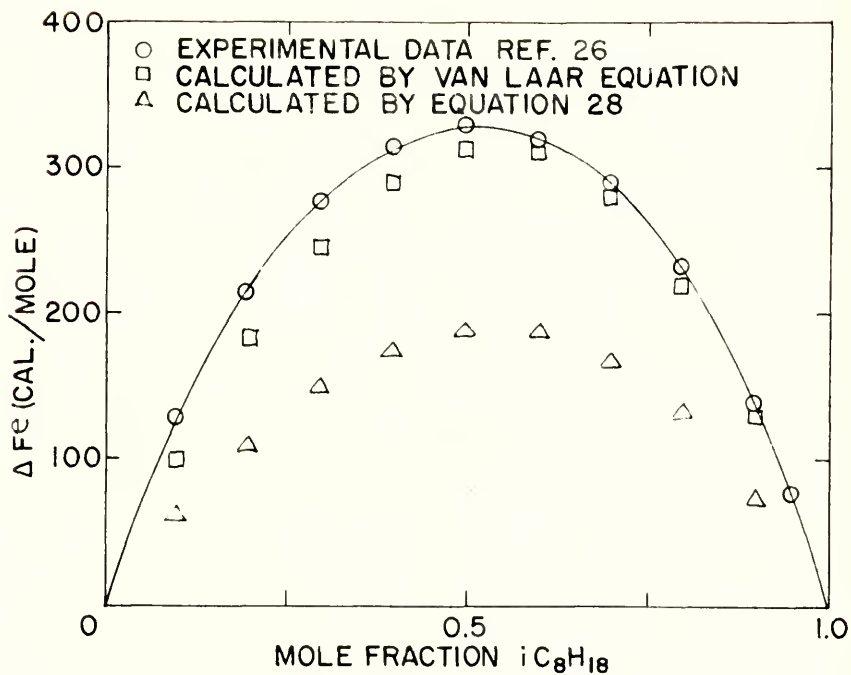


FIGURE 20. EXCESS FREE ENERGY OF MIXING
SYSTEM: C_7F_{16} - iC_8H_{18} AT 30°C.

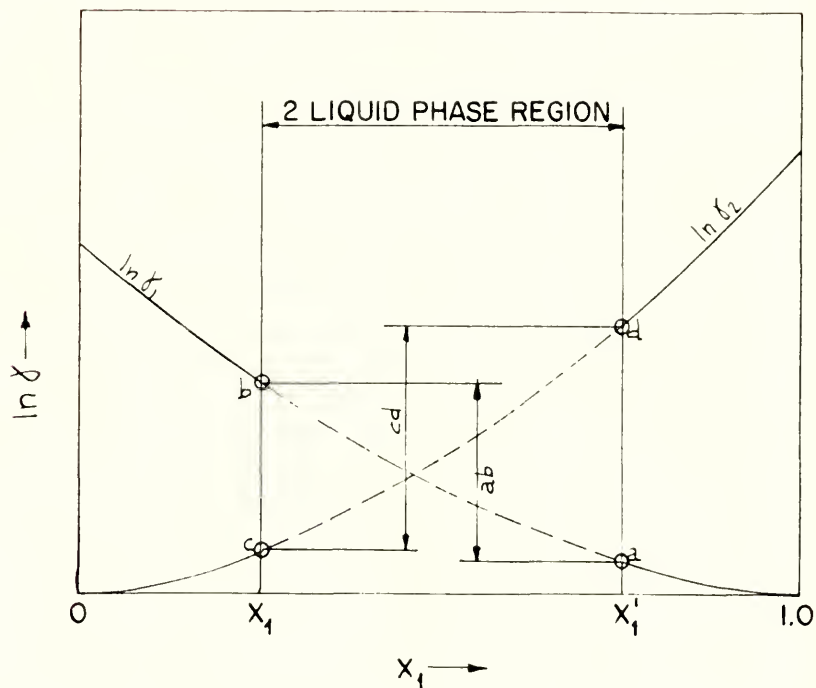


FIGURE 21. VAN LAAR ACTIVITY COEFFICIENTS

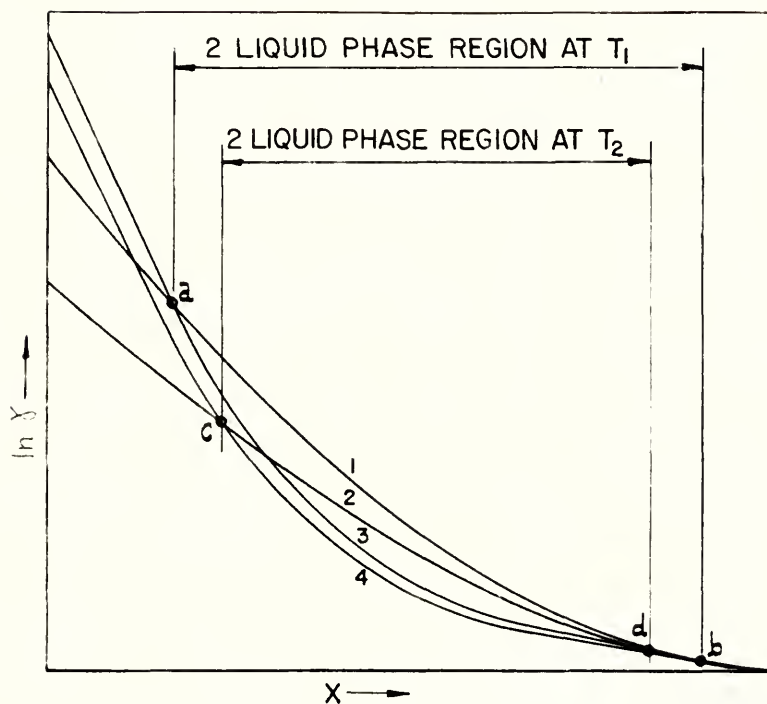


FIGURE 22. VAN LAAR ACTIVITY COEFFICIENTS
TEMPERATURE DEPENDENCE

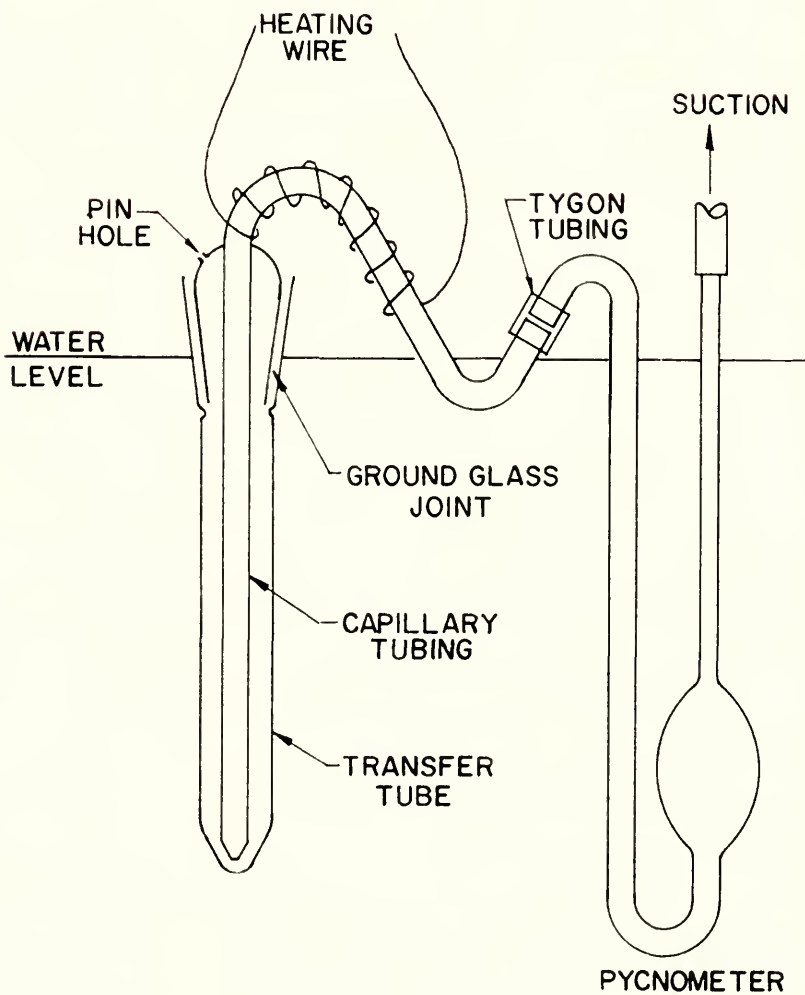


FIGURE 23. PYCNOMETER FILLING ARRANGEMENT

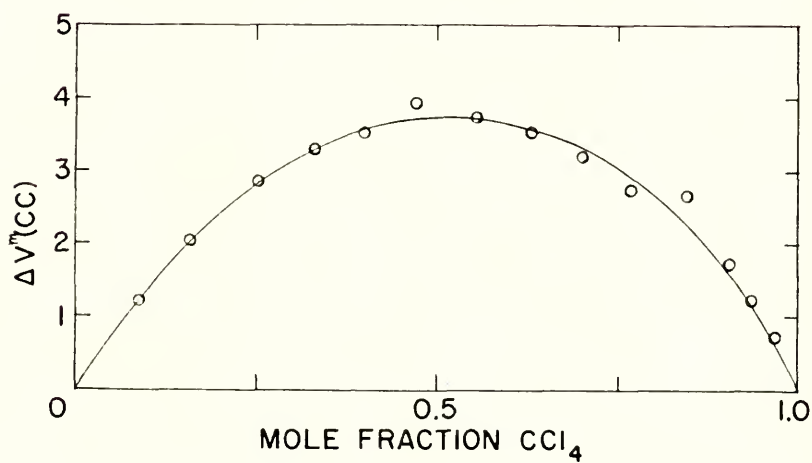


FIGURE 24. VOLUME CHANGE ON MIXING
SYSTEM: $\text{C}_8\text{F}_{16}\text{O}-\text{CCl}_4$ AT 50°C .

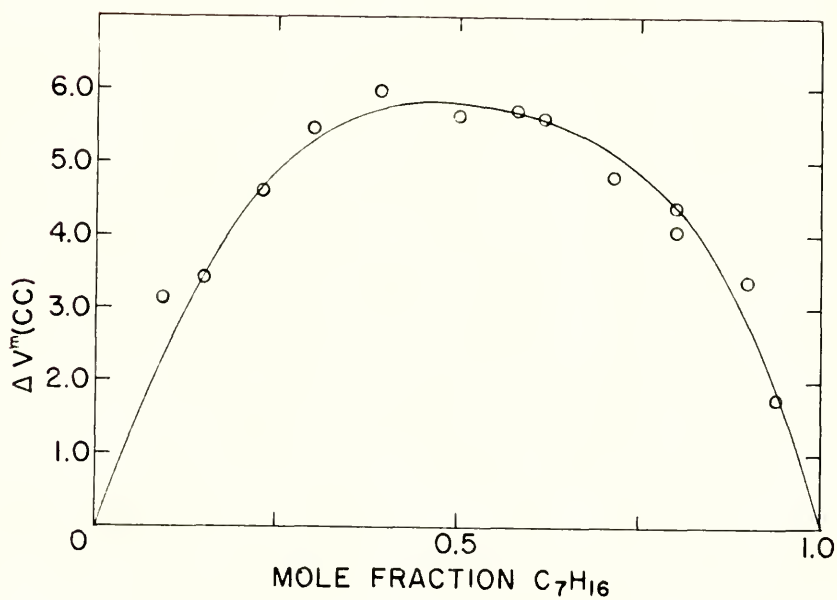


FIGURE 25. VOLUME CHANGE ON MIXING
SYSTEM: $C_7F_{16}-C_7H_{16}$ AT $50^\circ C$.

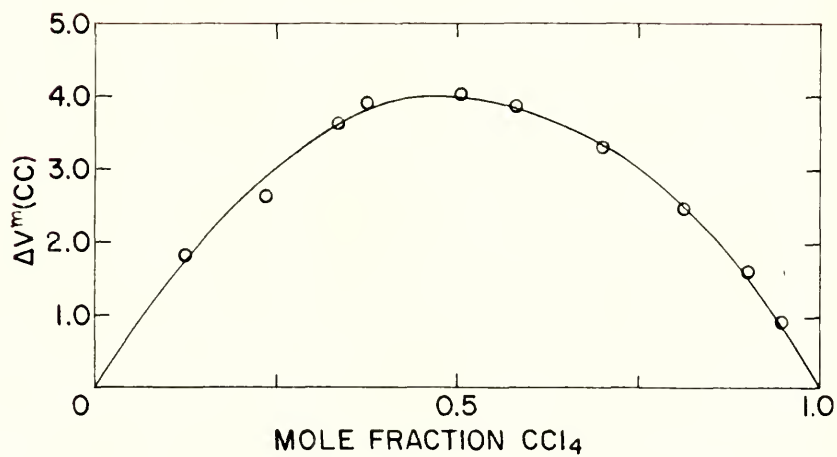


FIGURE 26. VOLUME CHANGE ON MIXING
SYSTEM: C_7F_{16} - CCl_4 AT 60°C .

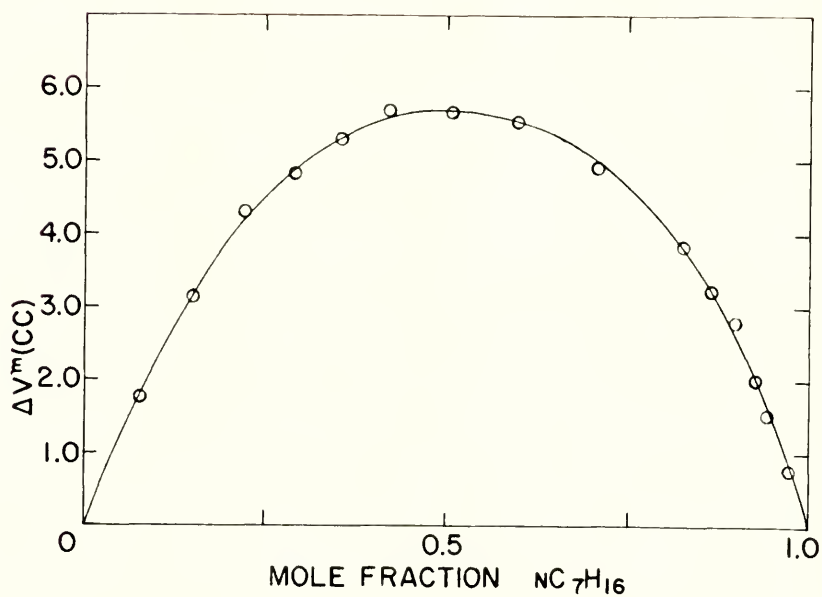


FIGURE 27. VOLUME CHANGE ON MIXING
SYSTEM: $C_8F_{16}O$ - nC_7H_{16} AT $50^\circ C$

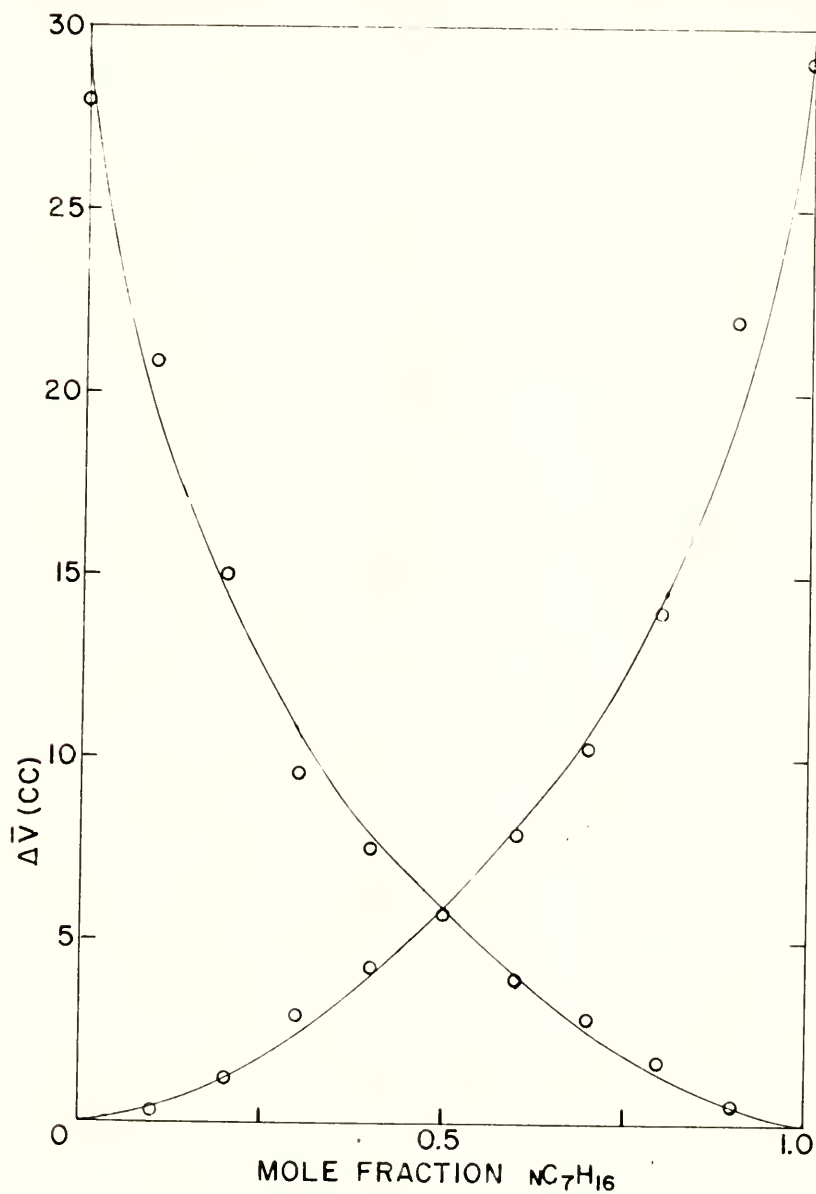


FIGURE 28. PARTIAL MOLAL VOLUME CHANGE
SYSTEM: $C_8F_{16}O$ - nC_7H_{16} AT $50^\circ C$.

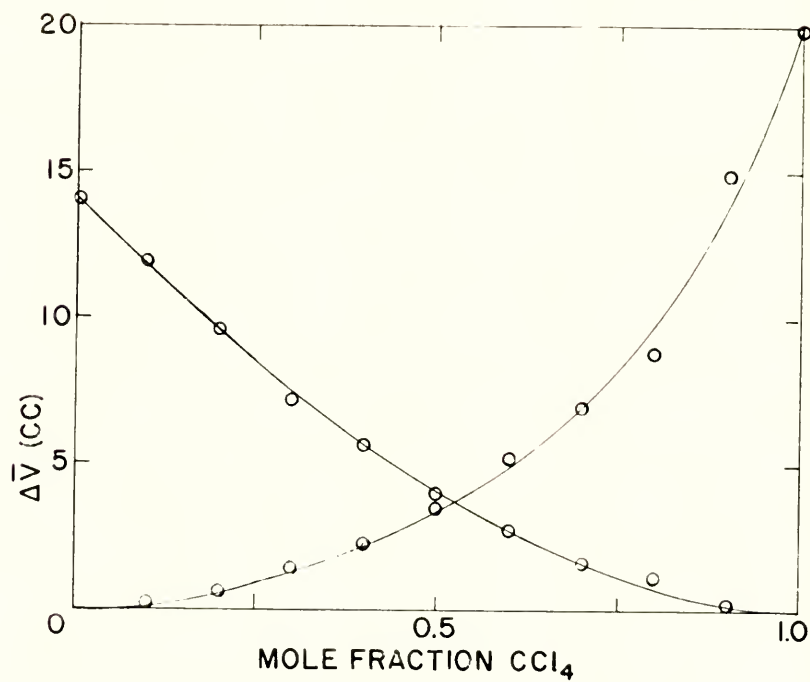


FIGURE 29. PARTIAL MOLAL VOLUME CHANGE
SYSTEM: $\text{C}_8\text{F}_{16}\text{O} - \text{CCl}_4$ AT 50°C .

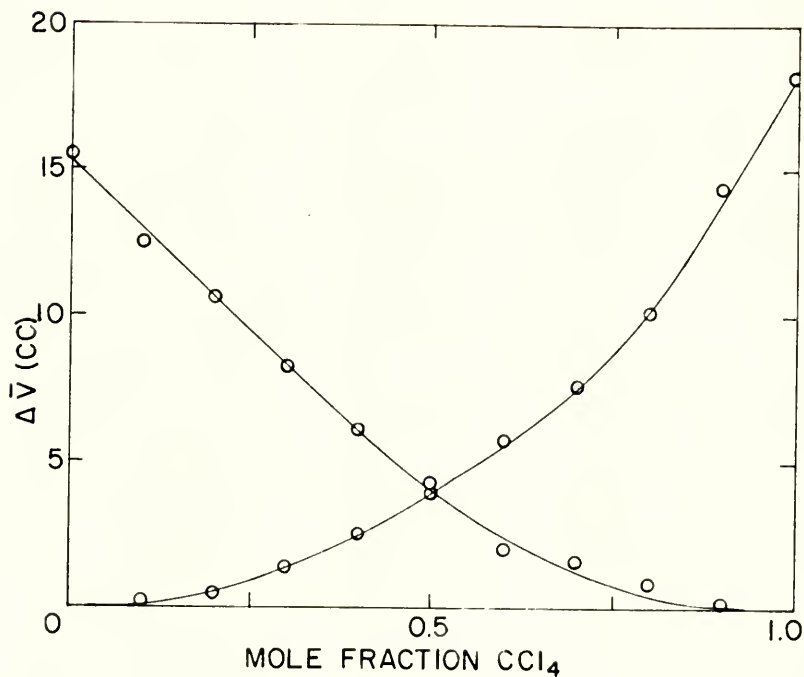


FIGURE 30. PARTIAL MOLAL VOLUME CHANGE
SYSTEM: C_7F_{16} - CCl_4 AT 60°C .

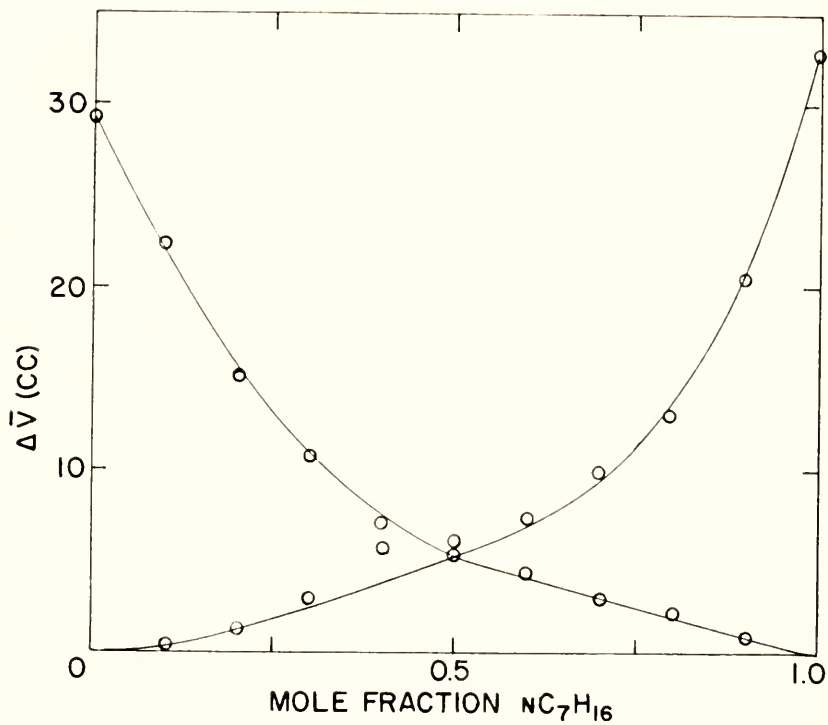


FIGURE 31. PARTIAL MOLAL VOLUME CHANGE
SYSTEM: C_7F_{16} - nC_7H_{16} AT $50^\circ C$

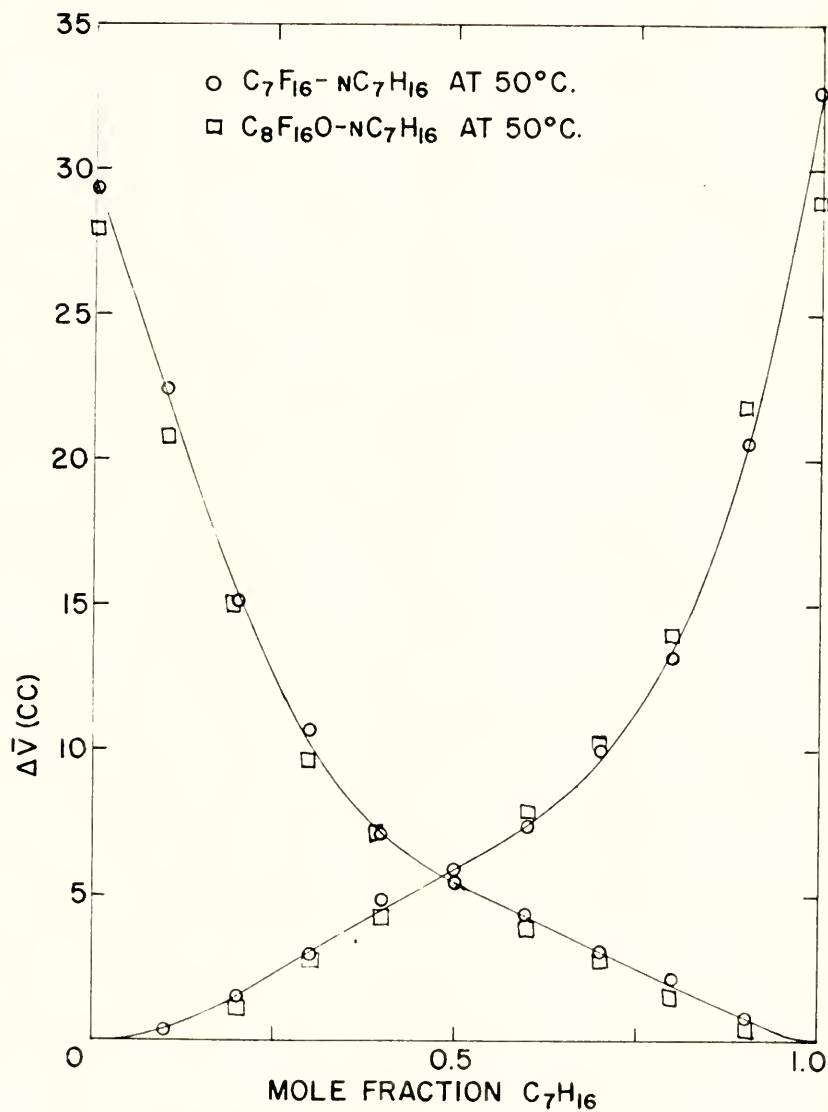


FIGURE 32. PARTIAL MOLAL VOLUME CHANGE

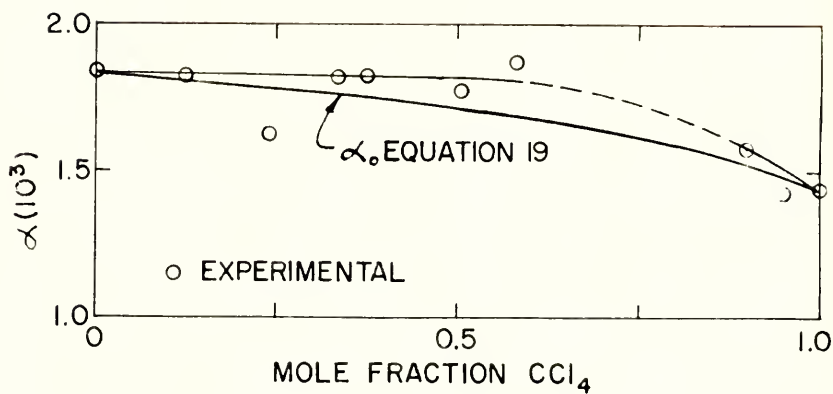


FIGURE 33. THERMAL COEFFICIENT OF EXPANSION
SYSTEM: C_7F_{16} - CCl_4

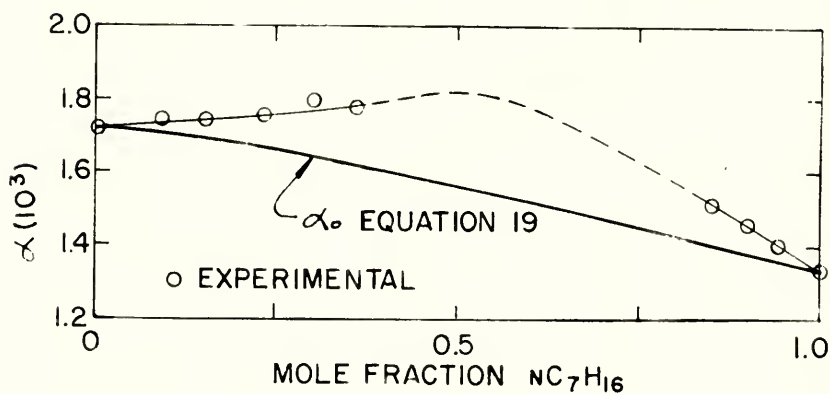


FIGURE 34. THERMAL COEFFICIENT OF EXPANSION
SYSTEM: C_7F_{16} - nC_7H_{16}

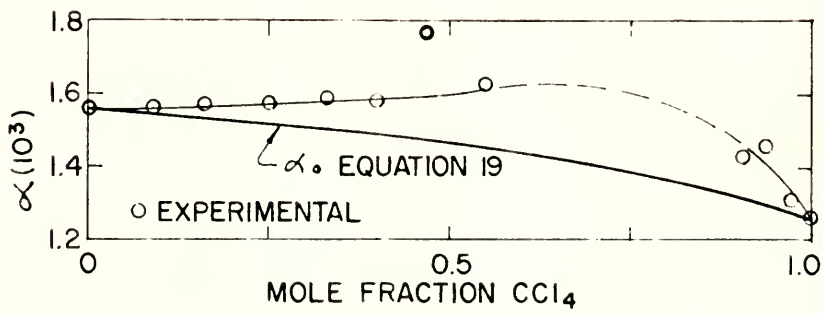


FIGURE 35. THERMAL COEFFICIENT OF EXPANSION
SYSTEM: $\text{C}_8\text{F}_{16}\text{O}-\text{CCl}_4$

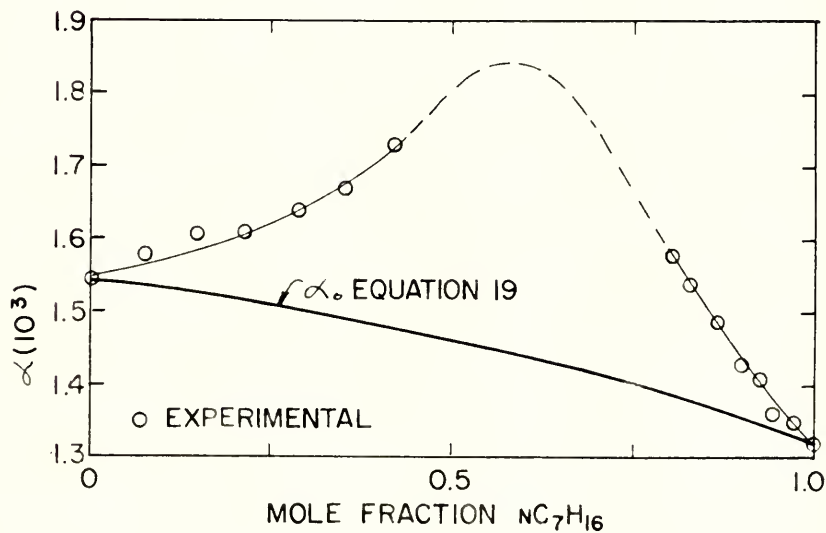


FIGURE 36. THERMAL COEFFICIENT OF EXPANSION
SYSTEM: $\text{C}_8\text{F}_{16}\text{O}-\text{nC}_7\text{H}_{16}$

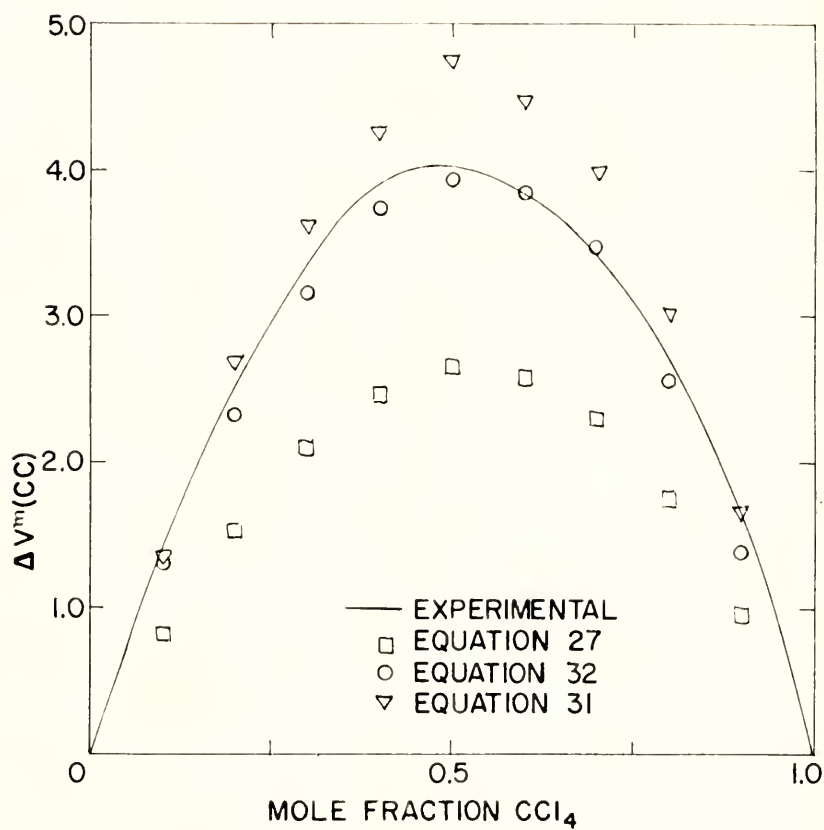


FIGURE 37. VOLUME OF MIXING
SYSTEM: $\text{C}_7\text{F}_{16}-\text{CCl}_4$

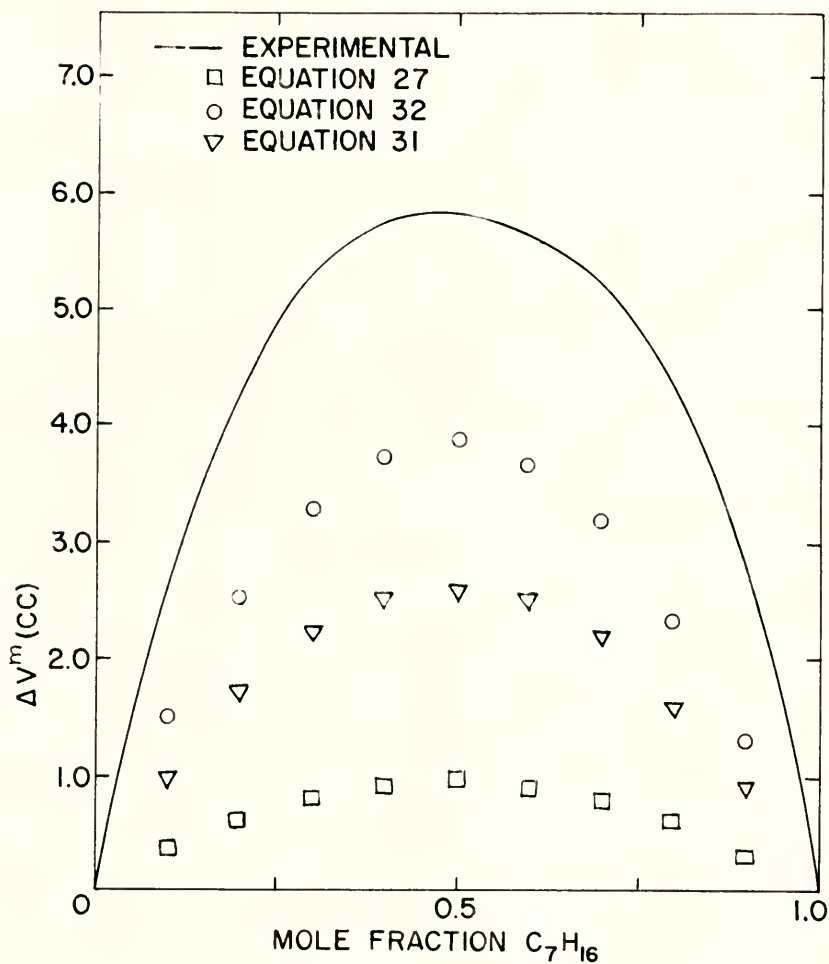


FIGURE 38. VOLUME OF MIXING
SYSTEM: C_7F_{16} - C_7H_{16}

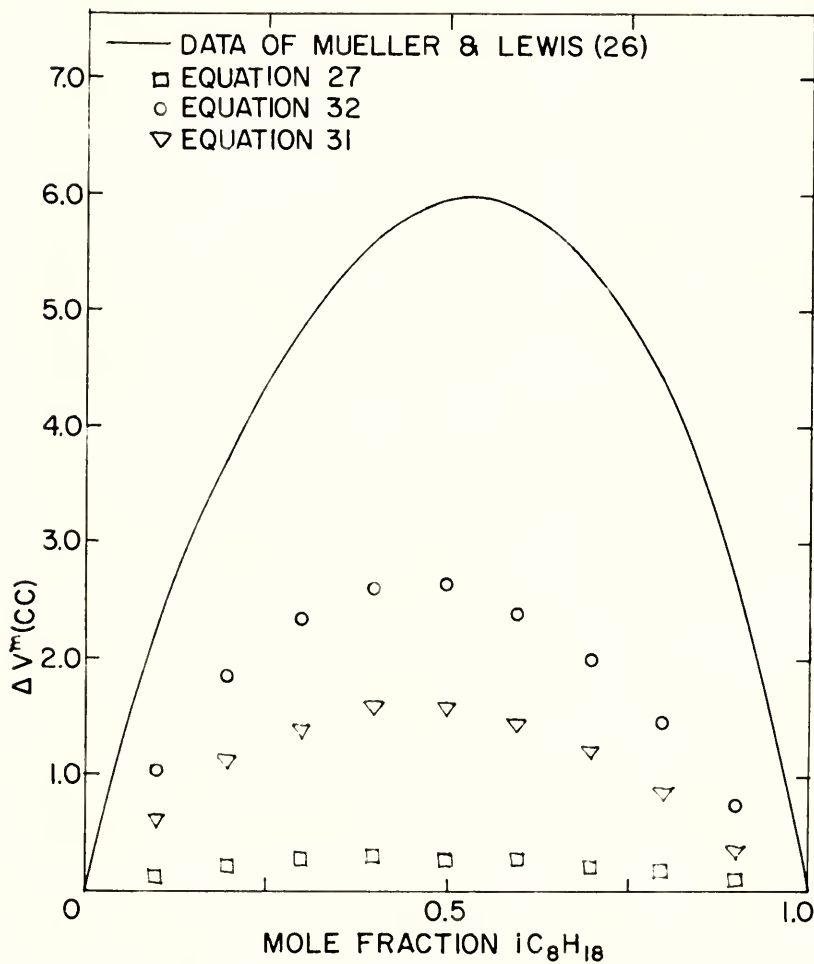


FIGURE 39. VOLUME OF MIXING
SYSTEM: C_7F_{16} - $i\text{C}_8\text{H}_{18}$

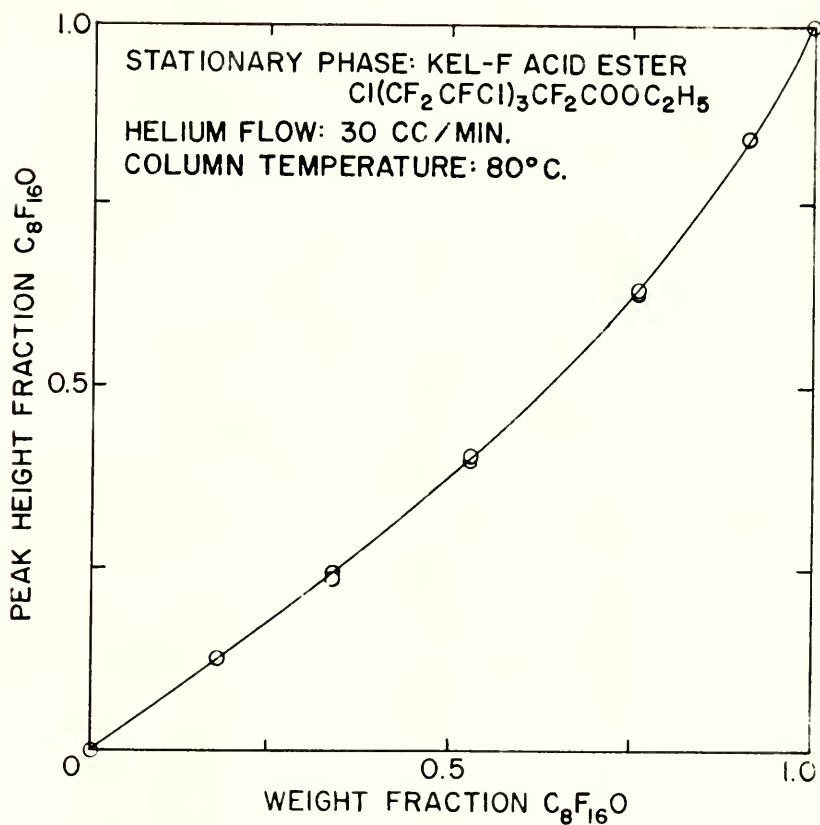


FIGURE 40. CALIBRATION OF SYSTEM $\text{C}_8\text{F}_{16}\text{O}$ - C_7F_{16}

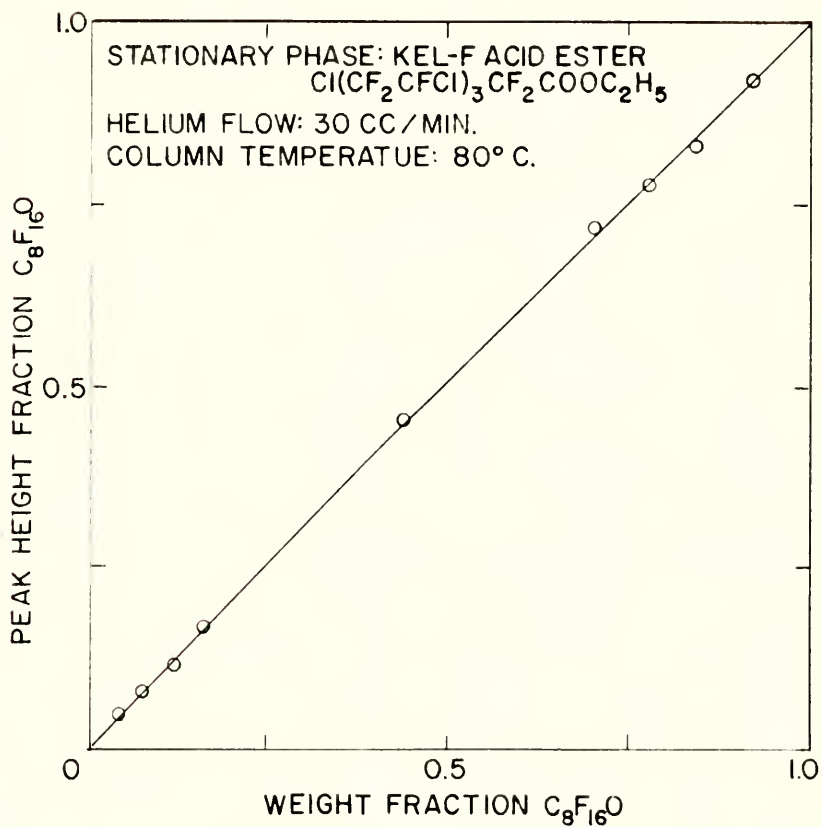


FIGURE 41. CALIBRATION FOR SYSTEM $\text{CCl}_4\text{-C}_8\text{F}_{16}\text{O}$

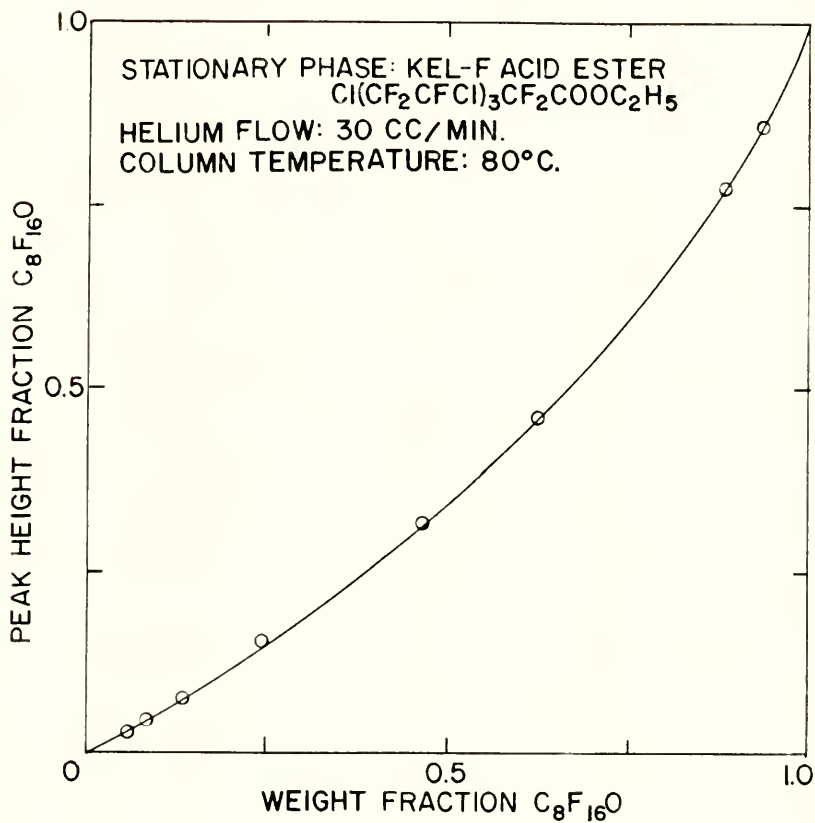


FIGURE 42. CALIBRATION FOR SYSTEM $\text{C}_8\text{F}_{16}\text{O}-\text{NC}_7\text{H}_{16}$

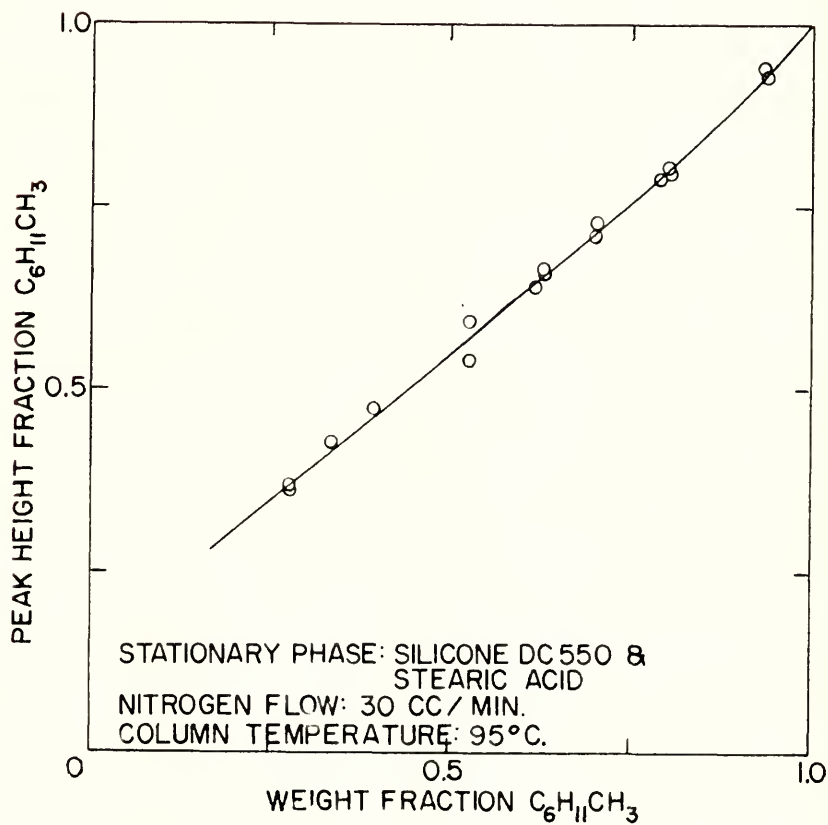


FIGURE 43. CALIBRATION FOR SYSTEM $C_6H_{11}CH_3$ - $C_6H_5CH_3$

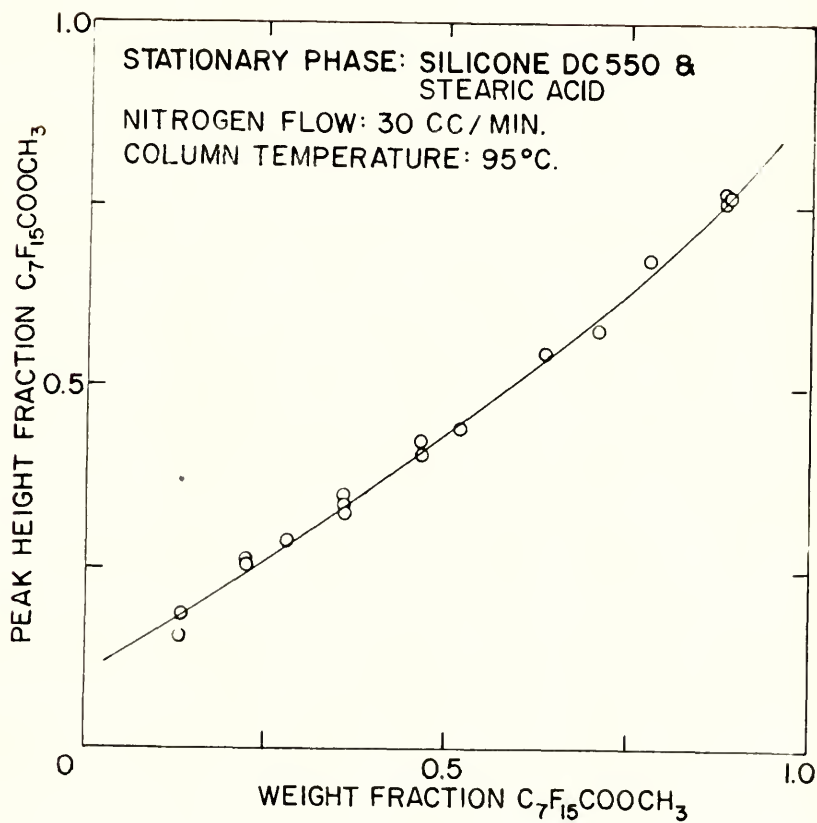


FIGURE 44. CALIBRATION FOR SYSTEM $C_6H_{11}CH_3$ - $C_7F_{15}COOCH_3$

FIGURE 45

PHASE DIAGRAM

SYSTEM C_7F_{16} - $C_8F_{16}O$ - CCl_4

AT 30°C.

NOTE: COMPOSITIONS ARE
IN WEIGHT FRACTIONS

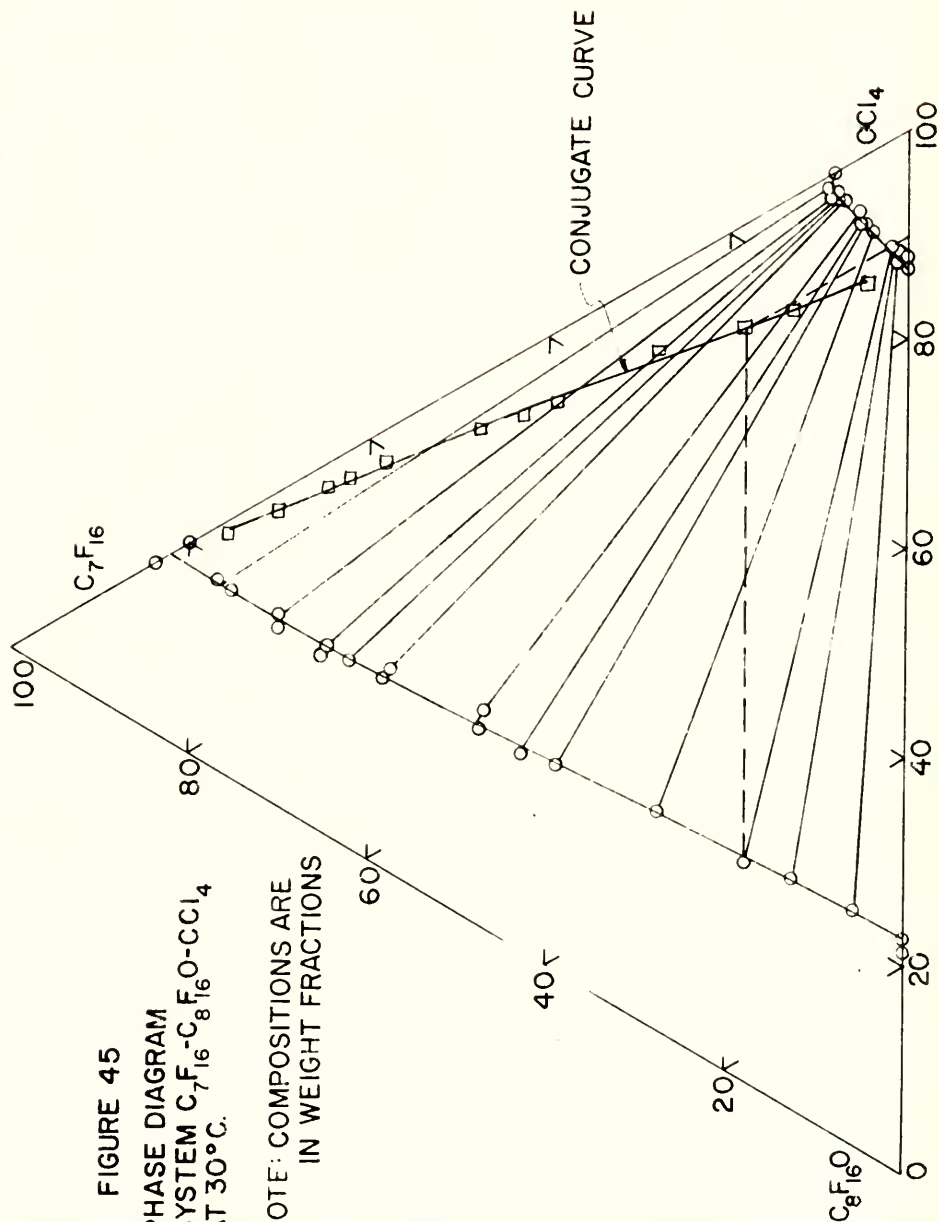


FIGURE 46

PHASE DIAGRAM

SYSTEM: C_7F_{16} - C_8F_{16} - nC_7H_{16}
AT $30^\circ C$.

NOTE: COMPOSITIONS ARE
IN WEIGHT FRACTIONS

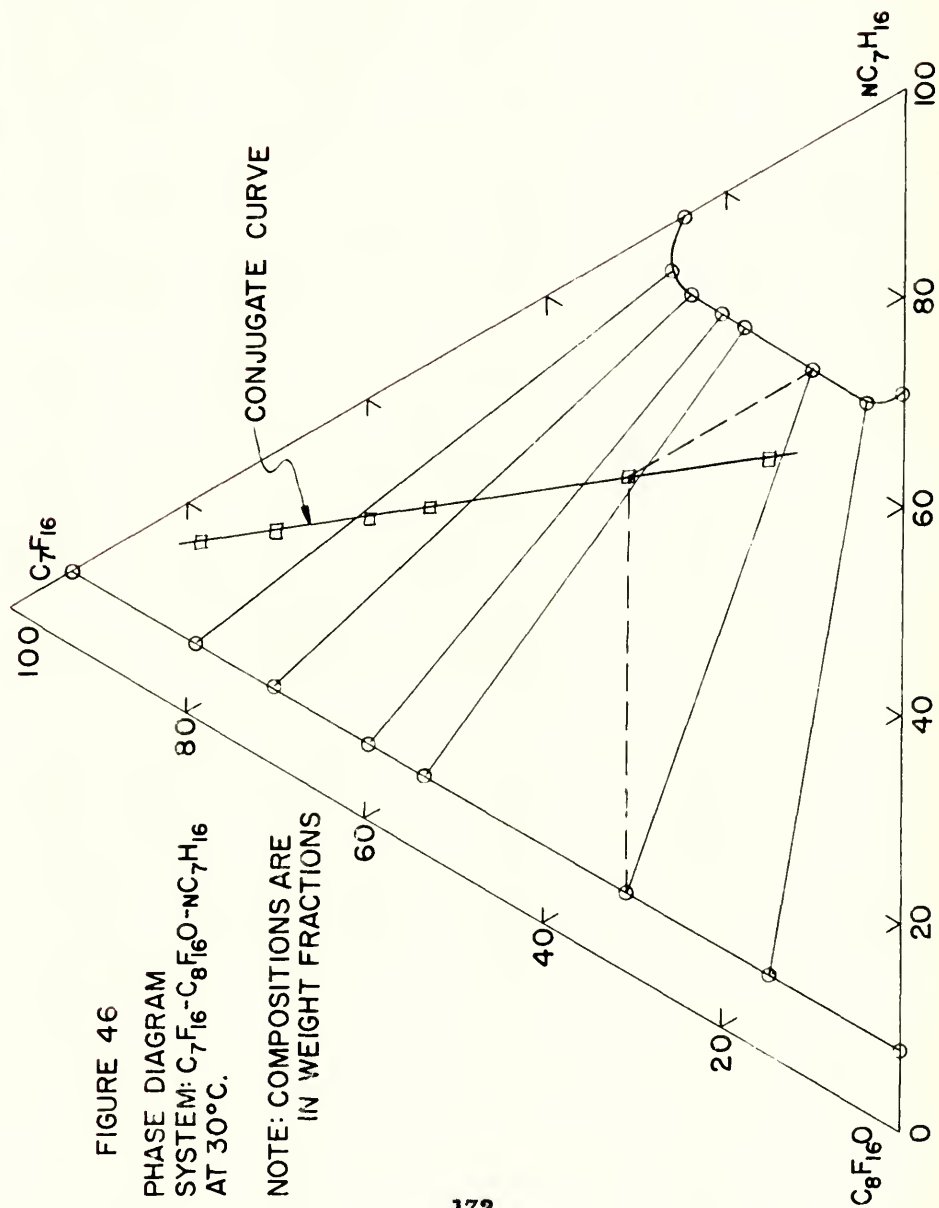


FIGURE 47

PHASE DIAGRAM

SYSTEM: $C_6H_5CH_3$ - $C_6H_{11}CH_3$ - $C_7F_{15}COOCH_3$ AT $25^\circ C$.

NOTE: COMPOSITIONS ARE IN WEIGHT FRACTIONS

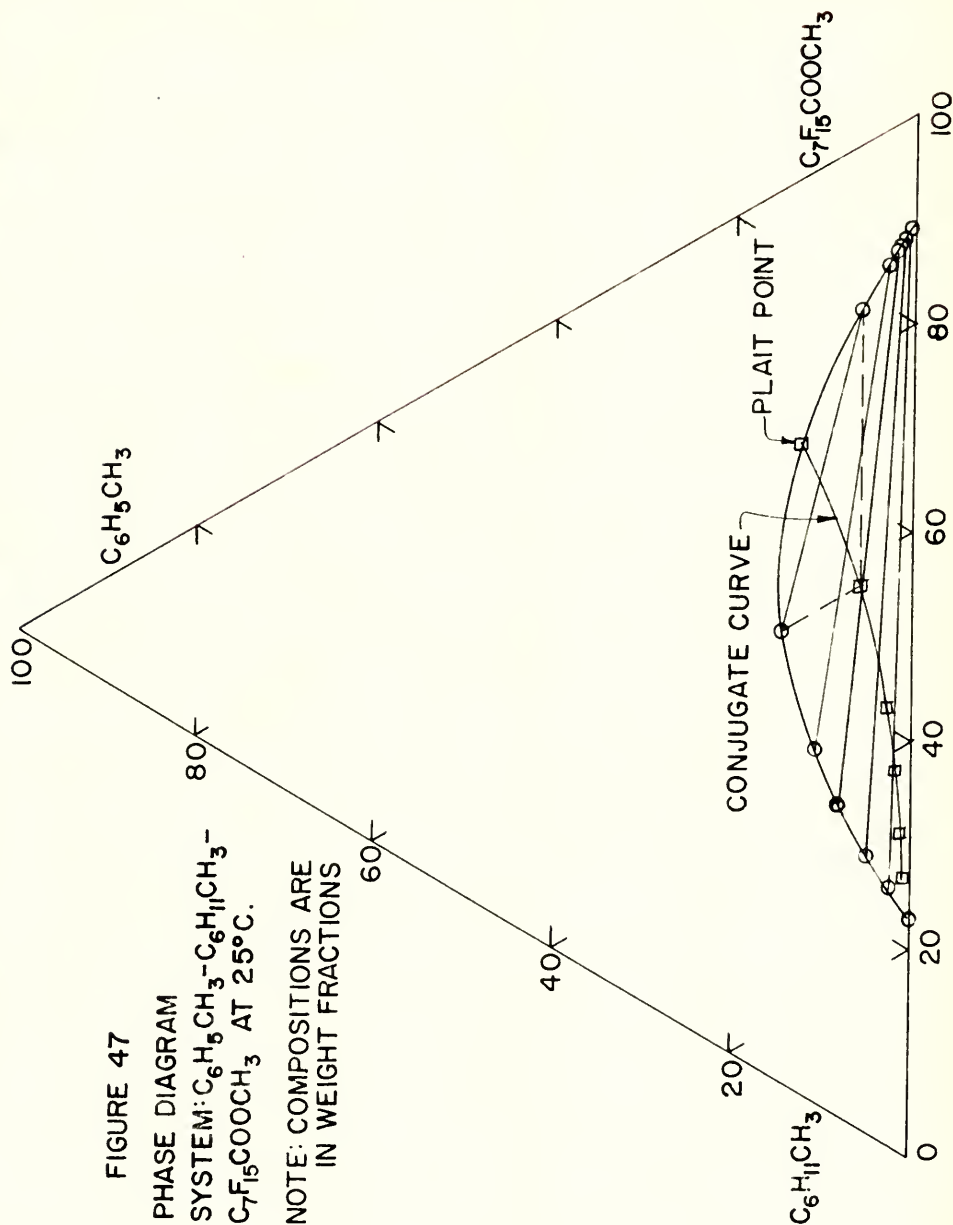
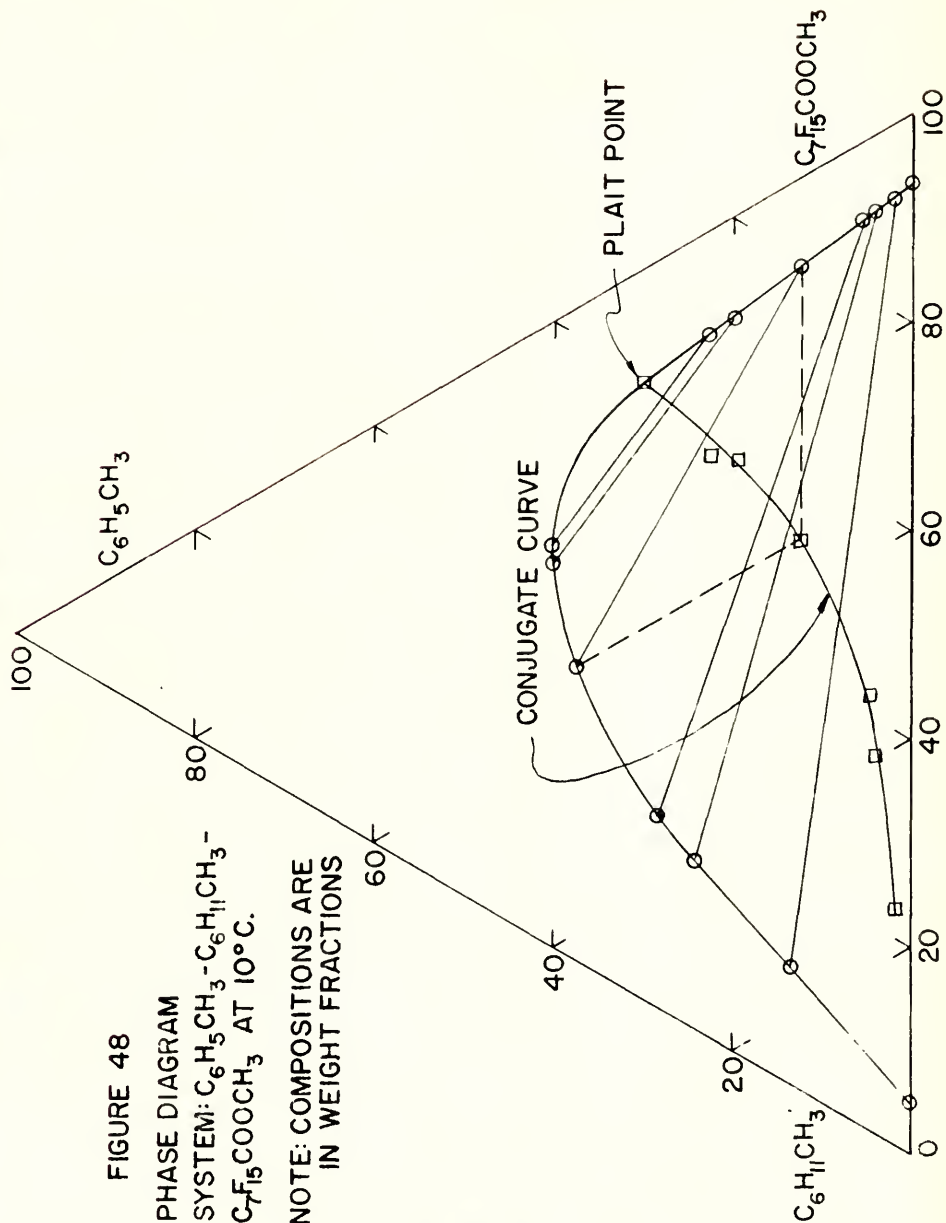


FIGURE 48

PHASE DIAGRAM

SYSTEM: $C_6H_5CH_3$ - $C_6H_{11}CH_3$ - $C_7F_{15}COOCH_3$ AT $10^\circ C$.

NOTE: COMPOSITIONS ARE
IN WEIGHT FRACTIONS



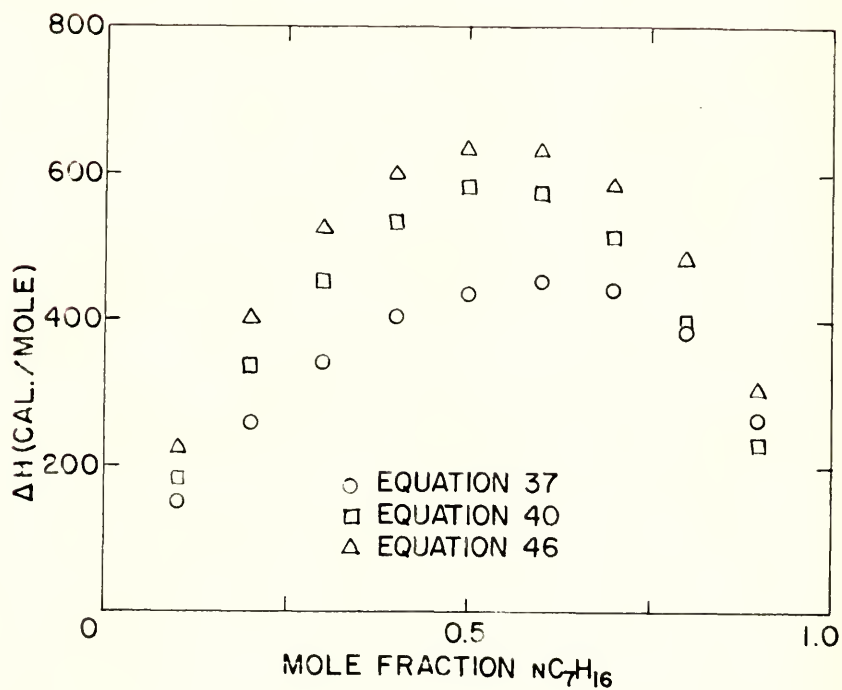


FIGURE 49. HEAT OF MIXING
SYSTEM: C_7F_{16} - nC_7H_{16} AT $50^\circ C$.

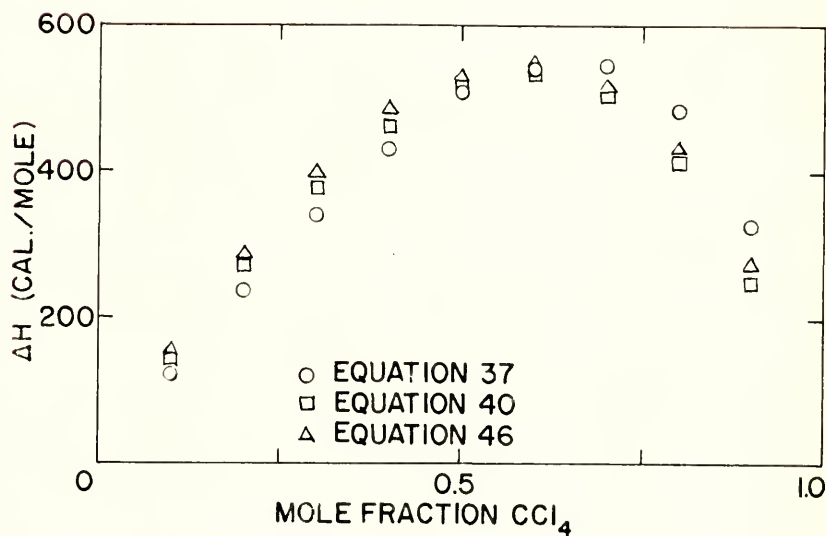


FIGURE 50. HEAT OF MIXING
SYSTEM: $\text{C}_7\text{F}_{16}-\text{CCl}_4$ AT 60°C .

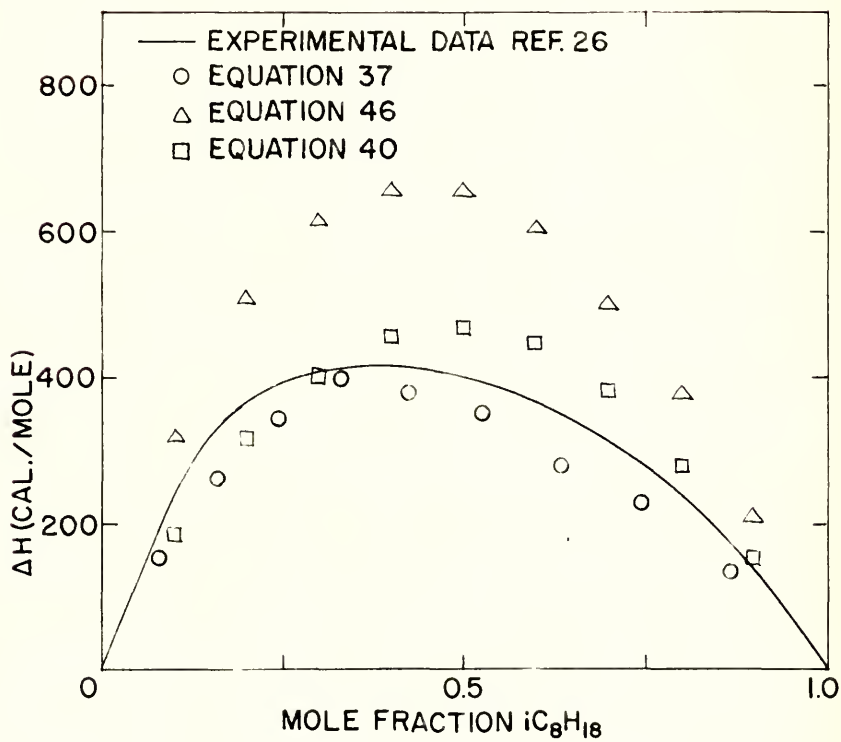


FIGURE 51. HEAT OF MIXING
SYSTEM: C_7F_{16} - iC_8H_{18} AT 30°C.

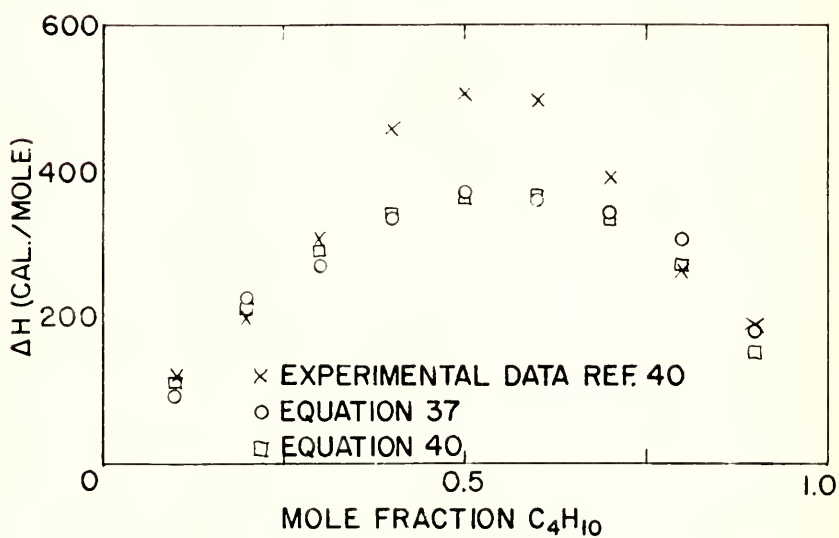


FIGURE 52. HEAT OF MIXING
SYSTEM: C_4F_{10} - C_4H_{10}

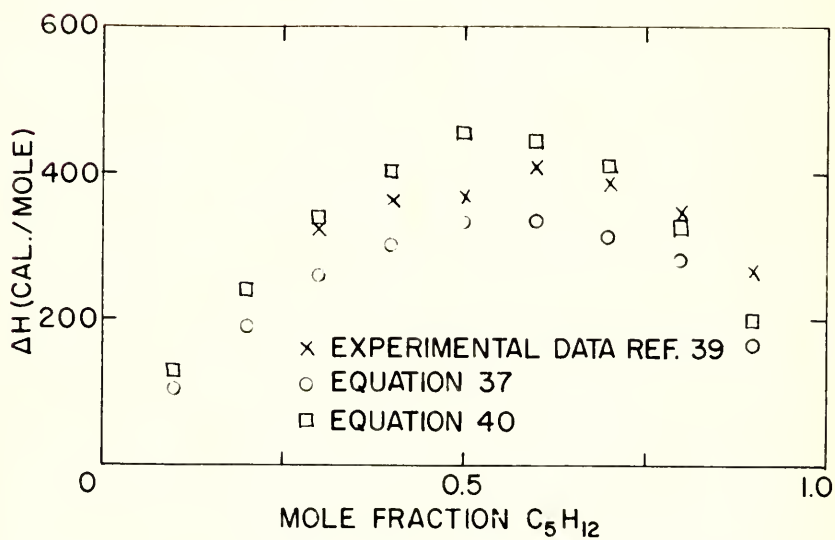


FIGURE 53. HEAT OF MIXING
SYSTEM: $C_5F_{12}-C_5H_{12}$

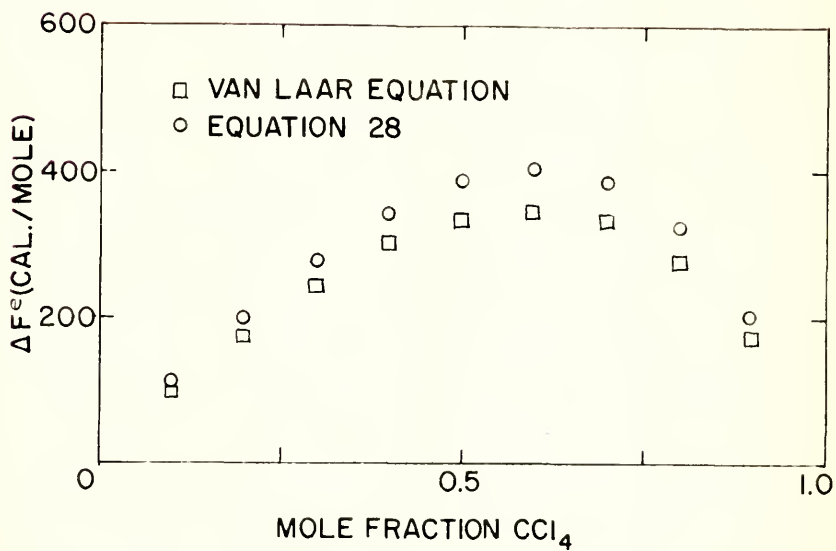


FIGURE 54. EXCESS FREE ENERGY OF MIXING
SYSTEM: C_7F_{16} - CCl_4

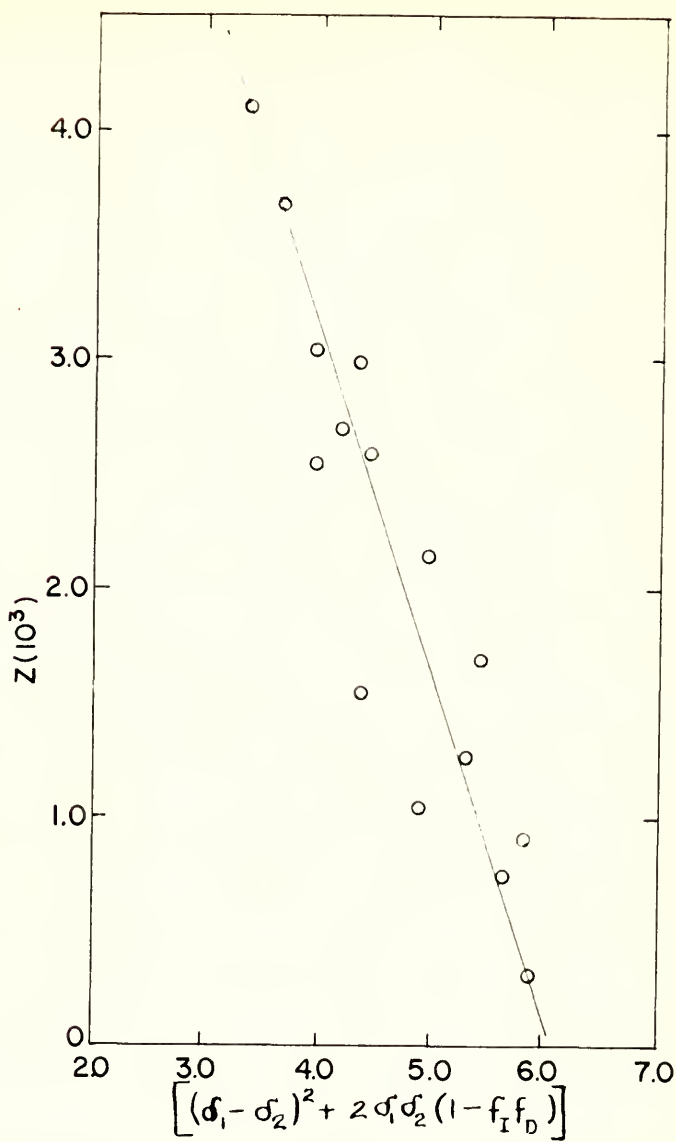


FIGURE 55. FREE ENERGY CORRELATION FOR
FLUOROCARBONS AND
PARAFFIN HYDROCARBONS

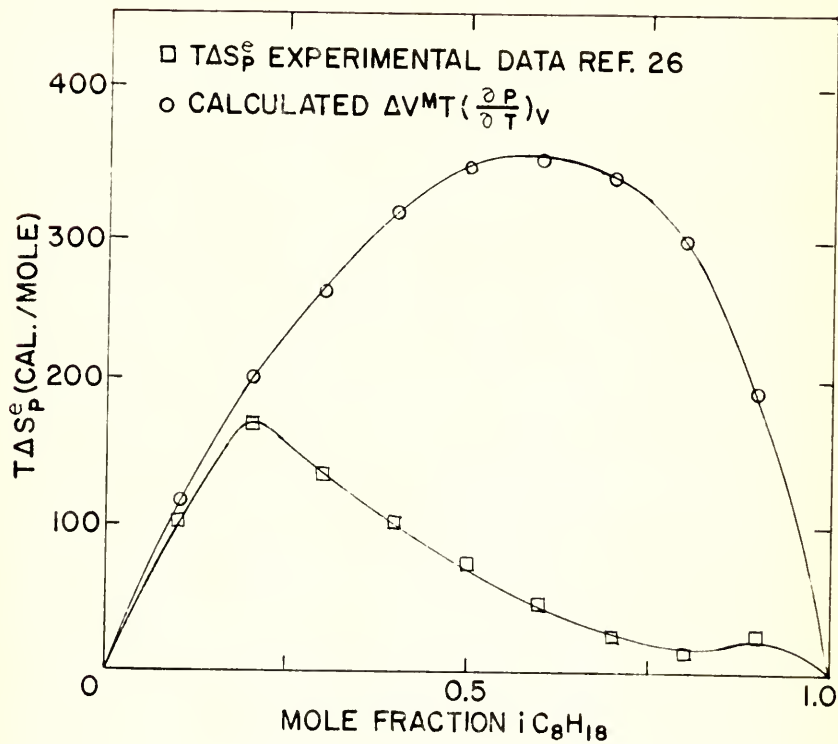


FIGURE 56. EXCESS ENTROPY OF MIXING
 SYSTEM: C_7F_{16} - iC_8H_{18} AT $30^\circ C$.

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BIOGRAPHICAL ITEMS

Benjamin G. Kyle was born in Atlanta, Georgia on December 4, 1927. He graduated from Druid Hills High School in Atlanta and entered The Georgia Institute of Technology in June, 1945. He graduated in June, 1950, with the degree of Bachelor of Chemical Engineering after serving one year in the Army (1946-1947).

Since graduation from the Georgia Institute of Technology he has worked for the U. S. Naval Shipyard in Charleston, South Carolina, and the Monsanto Chemical Company. In June, 1953 he entered the graduate school of the University of Florida where he received the degree of Master of Science in Engineering in January, 1955. He is a member of the Phi Kappa Phi honor society and the American Chemical Society.

This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Engineering and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

February 1, 1958

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Dean, College of Engineering

Dean, Graduate School

Max L. Tjerner
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